The Crystal Structure of $(NH_4)_2SbCl_5$

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$(NH_4)_2SbCl_5$ has been investigated by X-ray methods. It is monoclinic, space group No. 12, $C2/m$-C_2^{3h} with 4 formula units in the unit cell. The cell dimensions are: $a = 11.9_8$ Å, $b = 7.7_9$ Å, $c = 11.9_7$ Å, $a = 114.7°$ and $V = 1003.2$ Å^3, the atomic coordinates are given on p. 130, and the interatomic distances in Table 3. The antimony and chlorine positions were determined from Patterson projections and by applying the "Vector Convergence Method". The parameters were refined by electron density projections, from which the ammonium positions also were discovered. The ammonium positions were checked from space considerations.

The structure is represented in Figs. 11, 12, 13, and 14. Antimony is surrounded by five chlorine at five of the corners of a distorted octahedron forming an isolated $SbCl_5^{2-}$ group. The chlorine and ammonium form together a distorted close-packing with some vacant positions.

The structure determinations of the antimony(III)oxide halogenides $Sb_4O_5X_2$ where X = Cl or Br (Edstrand [1]), SbOCl (Edstrand [2]) and two other oxide halogenides with the idealized formulae $Sb_8O_{10}(OH)_2X_2$ where X = Cl, Br or I and $[Sb_8O_8(OH)_4]Cl_{2+x}[(OH)_{2-x}(H_2O)_{1+x}]$ (Edstrand [3]) have made it seem of interest to investigate the distances between trivalent antimony and the halogenide ions in the solid state, and also to obtain some more information regarding the coordination of trivalent antimony. In SbOCl there are two different types of Sb—Cl distances, one of the magnitude 2.4 Å and the other of the magnitude 3 Å. In $Sb_4O_5Cl_2$ we have only Sb—Cl distances of the magnitude 3 Å and larger. The distance of about 2.4 Å is of the same magnitude as the Sb—Cl distances found for $SbCl_3$ in the gas phase. Gregg, Hampson, Jenkins, Jones, and Sutton [4] found it to be 2.37 ± 0.02 kX by electron diffraction methods, and Kisliuk [5] found it to be 2.325 ± 0.005 Å by microwave methods.

Trivalent antimony seems to have different coordination numbers in different compounds. We shall here give a short review, which is not supposed to be complete, of the coordinations which have been found.

3-Coordination.

A more or less regular trigonal pyramid with antimony at the top: $SbCl_3$, $SbBr_3$, and SbI_3 in the gas phase [4,6], SbF_3 in the solid state [7], KSb_4F_{13}[8], Sb_2O_3 cubic [9,10] and orthorhombic [11], $ZnSb_2O_4$[12], Tetrahedrite Cu_3SbS_3[13,14], and Wolfsbergite $CuSbS_2$[15,16].

In the following compounds there are Sb(III) atoms with different coordination numbers, one of which is three: $Sb_4O_5Cl_2$ and $Sb_4O_5Br_2$[1], $SbOCl$[2], Sb_2S_3[16,17] and the isotypic Sb_2Se_3[18], and Berthierite $FeSb_2S_4$[19].

4-Coordination.

I. Tetrahedral coordination: Berthierite $FeSb_2S_4$[19].

II. A square pyramid with antimony at the top: Nadorite $PbSbO_2Cl$[20].

III. A deformed trigonal bipyramid with antimony in the centre and with one of the equatorial corners unoccupied: $Sb_4O_5Cl_2$ and $Sb_4O_5Br_2$[1], $SbOCl$[2], $Sb_8O_{10}(OH)_2X_2$ where X = Cl, Br, or I[3], and $[Sb_8O_8(OH)_4]Cl_{2+x}[(OH)_{2-x}(H_2O)_{1+x}]^3$.

IV. A deformed trigonal bipyramid with antimony in the centre and with one of the tops unoccupied: $CsSb_2F_7$[21].

5-Coordination.

A more or less regular octahedron with antimony in the centre and with one of the corners unoccupied: K_2SbF_5[22], $KSbF_4$[23], and $NaSbF_4$[24]. In these papers there are also discussions of the different coordinations found in some complex antimony(III)fluorides. It seems as if half of the antimony atoms in Sb_2S_3[16,17,25] have a coordination which can be interpreted as a 5-coordination of this type.

6-Coordination.

A more or less regular octahedron with trivalent antimony in the centre: $(NH_4)_2SbBr_6$, Rb_2SbCl_6, and Rb_2SbBr_6[26], Sb_2O_4 and $SbTaO_4$[27], and the idealized structure for Miargyrite $AgSbS_2$[28].

8-Coordination.

Around the trivalent antimony in Sb_3O_6OH[29].

9-Coordination.

In $SbSX$[30] and the isotypic $SbSeX$[31] where X = Br or I. There is, however, close contact between Sb and only some of the 9 anions. To us the constitution of the double bands of Sb, S, and X seems to suggest 5-coordination.

In some of the examples the positions of the light atoms might be a little uncertain on account of the difficulty of locating them from the X-ray data and, accordingly, there might also be some uncertainty in the coordination number. In the cases of the coordination number 3, the results might have been influenced by a preconception that this should be the normal coordination of trivalent antimony.

For the investigation of antimony-halogen distances in the solid state it seemed more convenient to use the complex antimony(III)halogenides than the simple halogenides, as some of the former are more stable in air than the

latter. It also seemed best to start with a compound with a fairly simple formula and which did not contain any water of crystallization.

After the structure determination of $(NH_4)_2SbCl_5$ was finished, there appeared a structure determination of the complex chloride $Cs_3Sb_2Cl_9$ by Yamatera and Nakatsu[32]. They report that it has the same type of structure as $Cs_3As_2Cl_9$[33]. From the data by Yamatera and Nakatsu it does not seem as if the coordinations of As and Sb are the same in these compounds. In $Cs_3As_2Cl_9$ there is only a pseudocoordination of six around As as it is in close contact with only three Cl atoms. The data for $Cs_3Sb_2Cl_9$, however, seem to indicate six coordination for Sb, and when calculating the Sb—Cl distances we find them to be 2.7 Å, which seems rather large. The structure determination has been based on powder data, but is going to be re-examined by single crystal methods according to a private communication by Dr. K. Nakatsu.

PREPARATION

Complex antimony(III)halogenides have been prepared by many investigators. A number of complex compounds in the system NH_4Cl-$SbCl_3$ are described in Gmelin [34]. $(NH_4)_2SbCl_5$ was first prepared by Jacquelain [35] who obtained it from an acid solution of the two salts in mole proportions according to the formula and described it as a dodeca-hedron derived from a regular hexahedral prism. Dehérain [36] prepared it by treating $SbCl_3 \cdot 2NH_3$ with hydrochloric acid and described it as yellow hexagonal plates.

In the present investigation, $SbCl_3$ and NH_4Cl were mixed in the mole proportions 3:4 in water with or without hydrochloric acid. The solution was then evaporated by heat or by means of a vacuum. When a solution was evaporated by heating to the beginning of crystallization a lot of hexagonal leaves precipitated during the cooling and after that needle-shaped crystals were formed as four-sided prisms. An example is: 0.646 g NH_4Cl was dissolved in 2.5 ml of 1 M HCl and then mixed with 2.06 g $SbCl_3$. This solution was then evaporated by boiling to a volume of about 1 ml. A few hexagonal plates precipita-ted. It was then kept in a vacuum desiccator above sulfuric acid for 20 hours during which the main part crystallized as four sided prisms. As far as we know these four sided prisms have not been described in the literature before, unless they are identical with a compound found by Poggiale [37]. He described it as crystallizing in beautiful rectangular prisms and ascribed to it the formula $3NH_3, HCl; SbCl_3 + 1.5H_2O$. We used these crystals for the structure determination. They were fairly stable in air, but on long exposure to air they were hydrolysed.

ANALYSIS

Since we could not take any reliable powder photographs on account of the hygroscopic character of the substance, we had to pick out a single crystal from each preparation and take a rotation or Weissenberg photograph for the identification of the substance. To be sure that these crystals really represented the main part we proceeded in the following way. In one preparation we obtained a very large crystal. From this crystal we cut off a small fragment, of which we took a Weissenberg photograph. The rest of the crystal we used for antimony analysis, and found that it gave the same result as the other preparations.

For the antimony determination, the substance was dissolved in hydrochloric acid and titrated with potassium bromate according to Smith and May [38] with naphthol blue-black as indicator. For the determination of chlorine, the substance was boiled with a concentrated solution of sodium carbonate in a platinum dish. After filtration the chloride was titrated by the Volhard method in the presence of nitrobenzene. Ammonium was determined according to Kjeldahl.

	Ammonium %	Antimony %	Chlorine %
Calc. for $(NH_4)_2SbCl_5$	10.77	36.33	52.90
Found	10.37, 10.57	36.47, 36.17	52.13, 51.86

UNIT CELL AND SPACE GROUP

Single crystals were selected. To avoid their decomposition they were coated with Apiezon grease, which protected them fairly well. Rotation and Weissenberg photographs were taken round two of the axes with Cu-radiation. We had the following series of Weissenberg photographs (double films): $h0l$, $h1l$, $h2l$, $h3l$, $h4l$, $hk0$, $hk1$, $hk2$, $hk3$, $hk4$, $hk5$, $hk6$, and $hk7$. Relative intensities of the reflections were estimated visually by comparison with an intensity scale obtained by exposing an interval of the zero layer line, containing a strong reflection, with different exposure times on a pack of four double films. They were then corrected for the Lorentz and polarization factors using the curves given by Kaan and Cole [39].

The crystals proved to be monoclinic with the b-axis coinciding with the needle-axis. The cell dimensions were determined from the Weissenberg photographs, as we could not obtain reliable powder photographs. Using $\lambda_{CuK\alpha_1} = 1.54051$ Å, where the α_1 and α_2 reflections were separated, and

$$\lambda_{CuK\alpha} = \frac{1}{3}(2\lambda_{\alpha_1} + \lambda_{\alpha_2}) = 1.54176 \text{ Å, where these reflections were not separated,}$$

we found the following values:

$a = 11.9_8$ Å, $b = 7.7_0$ Å, $c = 11.9_7$ Å, $\beta = 114.7°$ and $V = 1003.2$ Å^3

If 4 formula units are assumed per unit cell, the density would be $d_{calc} = 2.22$, we found $d_{obs} = 2.26$, 2.24.

The density of the crystals was determined from the loss of weight in carbon tetrachloride, as this liquid was found not to decompose the crystals. The density of carbon tetrachloride was taken from Beilstein [40].

In the Weissenberg photographs all reflections with $(h + k)$ odd are systematically absent, which is characteristic of the space groups No. 12, $C2/m—C_{2h}^3$, No. 5, $C2—C_2^3$, and No. 8 $Cm—C_s^3$ [41]. To try to decide between these three space groups, we applied the method of intensity statistics [42, 43] to the zero zones $h0l$ (see Fig. 1) and $hk0$ (see Fig. 2). It is apparent that the intensity distributions in both cases seem to indicate symmetry centres in
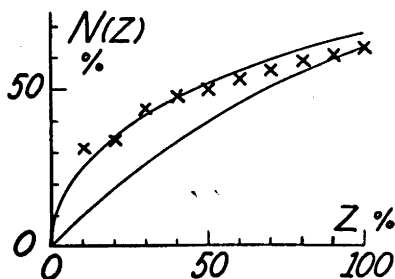

Fig. 1. Intensity statistics for h0l. × represents the experimental intensity distribution compared with the theoretical centric distribution (upper curve) and the theoretical acentric distribution (lower curve).

Fig. 2. Intensity statistics for hk0. × represents the experimental intensity distribution compared with the theoretical centric distribution (upper curve) and the theoretical acentric distribution (lower curve).
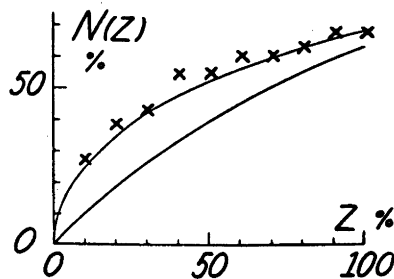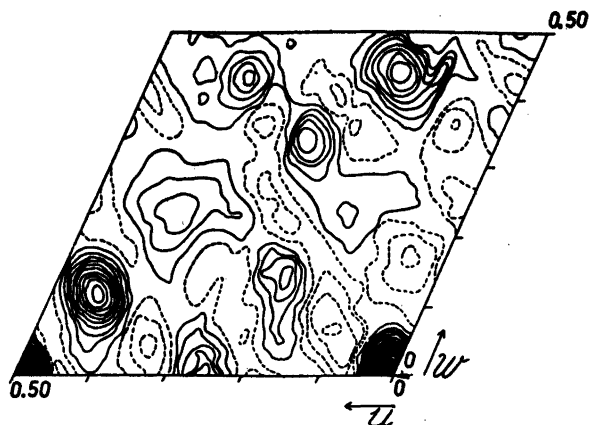
Fig. 3. P (UpW). Contours at an interval of 200 arbitrary units. Negative values dotted.

the projections, and thus it appeared reasonable to assume the space group to be No. 12, $C2/m$—C_{2h}^3, since this is the only one which has symmetry centres in both projections.

PATTERSON SYNTHESES AND VECTOR CONVERGENCE DIAGRAMS

It seemed probable that the positions of the four antimony atoms would be found from Patterson projections. The calculated $P(UpW)$-projection is given in Fig. 3 and the $P(UVp)$-projection in Fig. 4. Considering the space group $C2/m$, the antimony atoms can be situated either in one of the fourfold positions or in a combination of two twofold positions. Combinations of the twofold positions $2(a) + 2(c)$, $2(a) + 2(d)$, $2(b) + 2(c)$, and $2(b) + 2(d)$ all require maxima of the weight 2 in the $P(UpW)$-projection at $u = 0$, $w = \frac{1}{2}$ and at $u = \frac{1}{2}$, $w = \frac{1}{2}$. As we can see there are practically no observed maxima at these coordinates, and thus it seems reasonable to exclude the combinations mentioned. Combinations of the twofold positions $2(a) + 2(b)$ and $2(c) + 2(d)$ require maxima of the weight 2 in the $P(UVp)$-projection at $u = 0$, $v = \frac{1}{2}$. The observed maximum is, however, one of the lowest in this projection, and
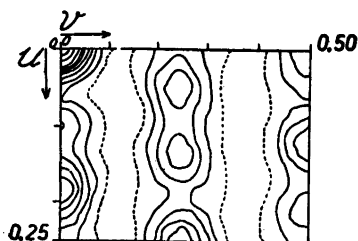

Fig. 4. P (UVp). Contours at an interval of 100 arbitrary units. Negative values dotted.

thus these combinations do not seem very probable. It therefore seems possible to exclude all the twofold positions. In the Patterson space $P(UVW)$ the fourfold positions give the following vectors:

I within 4(e) and 4(f) of weight 4	A	$0,\frac{1}{2},0$	
	B	$\frac{1}{2},\frac{1}{2},0$	
	C	$\frac{1}{2},0,0$	
II within 4(g) and 4(h) of weight 4	A	$\frac{1}{2},\frac{1}{2},0$	
of weight 2	B	$\pm (0,2y,0)$	
	C	$\pm (\frac{1}{2},\frac{1}{2} + 2y,0)$	
III within 4(i) of weight 4	A	$\frac{1}{2},\frac{1}{2},0$	
of weight 2	B	$\pm (2x,0,2z)$	
	C	$\pm (\frac{1}{2} + 2x,\frac{1}{2},2z)$	

As the maximum in the $P(UVp)$-projection corresponding to the vector **IA** is among the lowest, it seems possible to exclude the positions 4(e) and 4(f). The only maximum corresponding to the vector **IIB** in $P(UVp)$, which is of reasonable height, is situated at the origin. As this corresponds to $y = 0$ or $\frac{1}{2}$, this would mean that the fourfold position corresponds to two twofold positions, which does not seem probable from what has been stated above.

We then have to consider only the position 4(i) and the corresponding vectors of group III, which ought to be among the highest maxima found in the projections. The vector **IIIB** corresponds to the following series of possible maxima in $P(UVp)$ with $u = 2x = 0, 0.1025, 0.1847, 0.2908, 0.3818, 0.5000, 0.6182, 0.7092, 0.8153, 0.8975, 1.000 \ldots\ldots$ where the maxima at $u = 0.1847$ and 0.8153 are the highest after that the origin. In $P(UpW)$ the two maxima next in height to that at the origin are at a) $u = 0.4403$, $w = 0.1198$, which corre-

Fig. 5. The xy-vector convergence diagram. Only the lowest positive contours in P (UVp) have been drawn. The centers of the peaks are marked with crosses, the size of which are proportional to the heights. One set of Patterson maxima is marked with full lines and the other with dotted lines. The finally accepted atomic positions are indicated at the points of convergence.
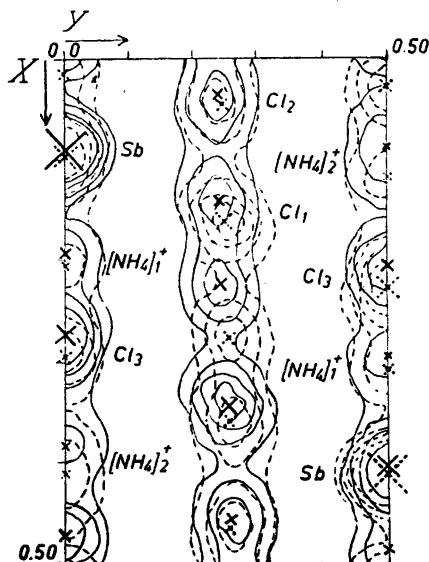
Fig. 6.   The xz-vector convergence diagram. Only the lowest positive contours in $P(UpW)$ have been drawn. The centers of the peaks are marked with crosses, the size of which are proportional to the heights. One set of Patterson maxima is marked with full lines and the other with dotted lines. The finally accepted atomic positions are indicated at the points of convergence.
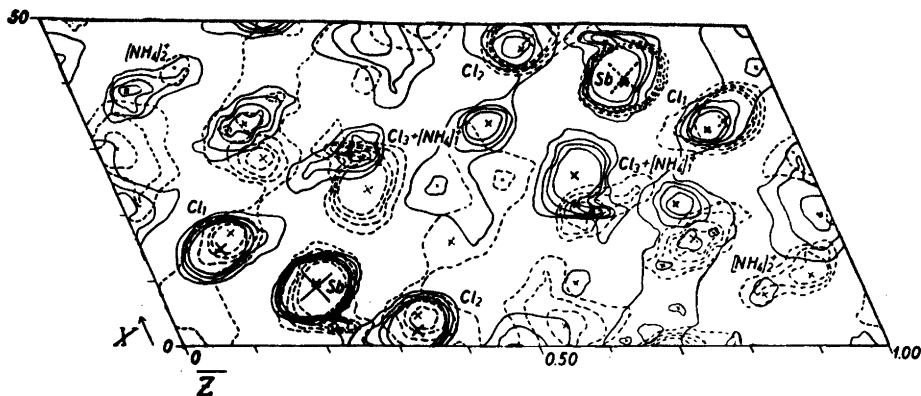
sponds to the following series of u-values: 0.4403, 0.9403, 0.0597, and 0.5597 and b) $u = 0.1743$, $w = 0.4422$, which corresponds to the following series of u-values: 0.1743, 0.6743, 0.3257, and 0.8257. We can see that the u-values of the series a) and b) which are sufficiently close to values in the series from $P(UVp)$ are $u = 0.1743$ and 0.8257 (in $P(UVp)$ 0.1847 and 0.8153). These two u-values with corresponding maxima give four different sets of atomic coordinates, which, however, can be transformed into each other by translations of $\frac{1}{2}$ along the axes. We now choose the coordinates $x = \frac{1}{2}(\frac{1}{2} \ 0.1743 + \frac{1}{2} \ 0.1847)$ $= 0.090$, $y = 0$, and $z = \frac{1}{2} \ 0.4422 = 0.221$ for Sb.

We also have to locate 20 chlorine atoms and 8 ammonium ions. It seemed quite probable that some of the other observed maxima in the Patterson projections would correspond to Sb—Cl vectors. This made it worth while to try the "Vector Convergence Method" described by Beevers and Robertson [44] on the projections starting with the previously found coordinates for Sb in 4(i). In this way we obtained the xy-projection in Fig. 5 and the xz-projection in Fig. 6. There are quite clear indications of the Cl-positions and it is also possible to guess something about the NH_4^+-positions. An interpretation of the diagrams gave the following set of approximate parameters, where the NH_4^+-positions are omitted since they did not seem quite certain.

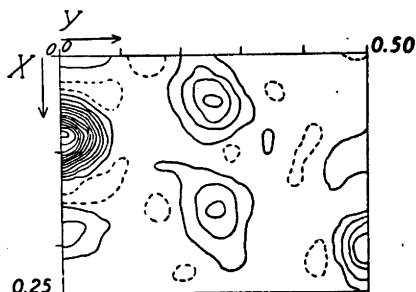|		x	y	z
Sb	in 4(i)	0.090	0	0.221
Cl_1	in 8(j)	0.159	0.245	0.120
Cl_2	in 8(j)	0.048	0.243	0.350
Cl_3	in 4(i)	0.286	0	0.360

Fig. 7. ϱ (XYp). Contours at an interval of 100 arbitrary units. Negative values dotted.

A rough calculation of the interatomic distances with these preliminary parameters showed that the distances were of reasonable magnitude, and that Sb is surrounded by 5 Cl at five of the corners of a deformed octahedron. Since a coordination of this type has been reported previously for the SbF_5^{2-}-ion in K_2SbF_5 by Byström and Wilhelmi [22], the Cl-positions seemed quite likely. It can be mentioned that $(NH_4)_2SbCl_5$ and K_2SbF_5 are not isomorphous.

FOURIER SYNTHESES

The best way to refine the parameters of antimony and chlorine and try to find the ammonium positions was by Fourier syntheses. In this case the coordination around antimony is of much more interest than the coordination around the ammonium ions, and thus it does not seem necessary to find the ammonium parameters with very large accuracy. The Fourier syntheses have been calculated with $F_{obs} = \sqrt{\dfrac{I}{Lp}}$ where F is the structure factor, I is the estimated intensity, Lp are the combined Lorentz and polarization factors. In all syntheses the value of $F(000)$ has been omitted. Correction for absorption has not been applied. The maxima have been located by the interpolation table given by Booth [45].
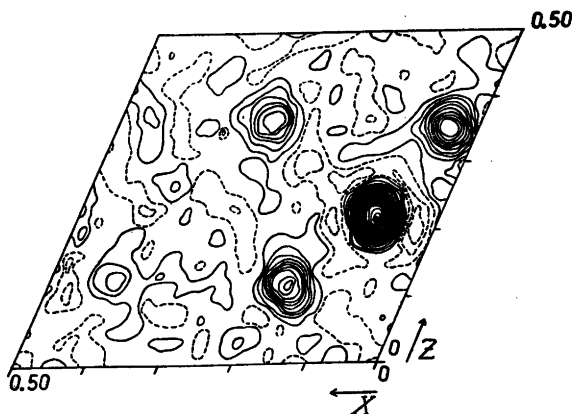

Fig. 8. ϱ (XpZ). Contours at an interval of 200 arbitrary units. Negative values dotted.

The refinement proceeded by successively calculating several $\varrho(XYp)$- and $\varrho(XpZ)$-projections, including more and more F-values. The final $\varrho(XYp)$-projection is given in Fig. 7, and the final $\varrho(XpZ)$-projection in Fig. 8. The antimony and chlorine peaks are clearly resolved, and we see that, in the $\varrho(XpZ)$-projection, the eightfold chlorine positions Cl_1 and Cl_2 are higher than the fourfold chlorine position Cl_3 as can be expected. There are also indications of the ammonium positions, which seem to be situated in the fourfold positions $4(i)$. One of them, $(NH_4^+)_1$, is quite clear in $\varrho(XYp)$ but is masked in $\varrho(XpZ)$ by Cl_3, since the two atoms are situated practically above each other. The $(NH_4^+)_2$-maximum in $\varrho(XpZ)$ is the maximum next in height to the Cl_3-peak. It is also found in $\varrho(XYp)$ but here it is rather low. We then arrived at the following set of parameters, where x_1 indicates the parameter from $\varrho(XpZ)$, x_2 the parameter from $\varrho(XYp)$, x_{mv} the mean value of the two, and $\triangle x = |x_1 - x_2|$.

		x_1	x_2	x_{mv}	y	z	$\triangle x$
4 Sb	in 4(i)	0.0860	0.0867	0.086$_3$	0	0.220$_8$	0.0007 = 0.008 Å
8 Cl$_1$	in 8(j)	0.1692	0.1650	0.16$_7$	0.24$_0$	0.11$_9$	0.0042 = 0.05
8 Cl$_2$	in 8(j)	0.0375	0.0492	0.04$_3$	0.24$_1$	0.35$_2$	0.0117 = 0.14
4 Cl$_3$	in 4(i)	0.2903	0.2937	0.29$_2$	0	0.36$_8$	0.0034 = 0.04
4 (NH$_4^+$)$_1$	in 4(i)	0.2097	0.1875	0.19$_9$	0	0.63$_3$	0.0222 = 0.27
4 (NH$_4^+$)$_2$	in 4(i)	0.4113	0.3931	0.40$_2$	0	0.12$_9$	0.0182 = 0.22

From the values of $\triangle x$ we obtain an approximate estimation of the accuracy of the x-parameters, and it seems probable that the accuracy of the y- and z-parameters is about the same if we measure them in Å units. The maximum value of $\triangle x_{Cl}$ is 0.14 Å, which seems to indicate that the Sb—Cl distances are accurate to within $\pm$ 0.25 Å, and the Cl—Cl distances to within

Fig. 9. Cut at $y = 0$ to locate NH_4^+. + projection of centre of Cl. ⊙ projection of centre of Sb. Full circle = forbidden area around Cl and dotted circle = forbidden area around Sb. There are room for the $8NH_4^+$ in two fourfold positions inside the areas marked I and II.
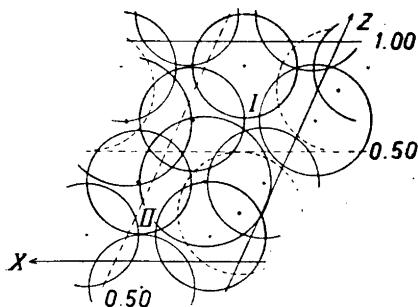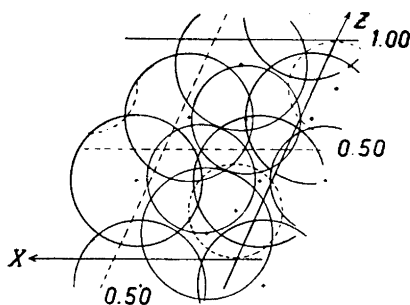

Fig. 10. Cut at $y = \frac{1}{4}$ to locate NH_4^+. + projection of centre of Cl. ⊙ projection of centre of Sb. Full circle = forbidden area around Cl and dotted circle = forbidden area around Sb. Here is no room for NH_4^+.

± 0.5 Å. Considering, however, that the distances $Sb—Cl_1$ and $Sb—Cl_2$ are equal (*cf.* Table 3) the real accuracy might be a little better than that stated above.

Because the parameters of the eight NH_4^+ are the least accurate, it is advisable also to ascertain their possible positions from space considerations. They can be situated either in two fourfold positions or in one eightfold position. The sum of ionic radii are $NH_4^+—Cl^-$ 3.24 kX (Goldschmidt, from Internationale Tabellen [46]). Not knowing much about the minimum distance between antimony and ammonium, we assumed it could not be shorter than 3 Å. Considering that the b-axis is 7.70 Å, and that there are mirror planes at $y = 0$ and $\frac{1}{2}$, the only possible y-parameters are $y = 0$, $y = \frac{1}{2}$, and y approximately 1/4. Spheres of appropriate radii, inside which no ammonium centers could occur, were considered around the chlorine and antimony centers. Cuts were made at $y = 0$, see Fig. 9, and at $y = 1/4$, see Fig. 10. We see that there is only room for the ammonium ions in the cut $y = 0$ inside the areas marked I and II. As the ammonium positions found from the Fourier projections fall inside these two areas, it seems justified to assume these positions. As the exact $NH_4^+—Cl$ distances are not of any particular interest in this case, we did not try to refine the ammonium parameters any further.

F-values were then calculated as

$$F_{calc} = const \left[f_{Sb}A_{Sb} + f_{Cl} \sum_{1}^{3} A_{Cl_i} + f_N \sum_{1}^{2} A_{NH_4^+} \right]$$

where f_{Sb}, f_{Cl} and f_N are the atomic scattering factors of antimony, chlorine and nitrogen with due consideration taken to their variation with Θ[46]. The calculated and observed F-values are given in Tables 1 (for $h0l$) and 2 (for $hk0$).

The reliability factor $R = \dfrac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ is 0.24 (0.27 without NH_4^+) for $h0l$ and 0.23 (0.27 without NH_4^+) for $hk0$ when only the observed reflections have been included. The values of R calculated with an without the NH_4^+-parameters also indicate that these positions are probable.

DISCUSSION OF THE STRUCTURE

As mentioned on p. 129 Sb is surrounded by five Cl at the corners of a deformed octahedron, where the sixth corner is unoccupied, giving an isolated $SbCl_5^{2-}$ group, see Fig. 11. This type of coordination has been postulated by Pauling [47] for an atom with five bonds and one unshared electron pair, which occupies the sixth corner. The distances in the $SbCl_5^{2-}$ group are: $Sb—4Cl$ (approximately in one plane) 2.6_2 Å and $Sb—Cl$ (opposite the empty corner) 2.3_6 Å. We see that the $Sb—Cl$ distance opposite the empty corner is shorter than the others and that the difference is perhaps too large to be explained entirely by the errors in the distances. As a comparison we have the following $Sb—Cl$ distances in the solid state: in Rb_2SbCl_6 2.47 ± 0.03 kX[26], in SbOCl 2.2_9 and 2.4_7 ± 0.3 Å². As to the distances in the gasphase see p. 122.

Table 1. Calculated and observed F-values of h0l for a

h	h00 F_c F_o	h01 F_c F_o	h02 F_c F_o	h03 F_c F_o	h04 F_c F_o	h05 F_c F_o	h06 F_c F_o	h07 F_c F_o
12	31 17	48 22	—36 35	—57 41				
10	13 28	52 53	16	—35 35	12	51 49		
8	—65 61	3	51 54	—85 69	—25 32	68 44	35 17	41 17
6	—35 46	3	71 79	9 17	—86 76	—45 44	22 32	43 33
4	—38 39	—128 150	103 126	109 130	—10 17	—10 17	—74 68	—10
2	22 30	—122 129	—98 108	42 60	72 76	—4	—18 36	—16 17
0			—97 93	—12	—62 80	36 50	—2 14	—90 95
—2		92 55	6	—27 30	12 14	50 54	38 47	—76 78
4		34 32	—58 62	14 22	—56 61	—2	164 148	9
6		17 14	58 76	24 37	—61 74	—100 106	9	68 80
8		4	—4 25	86 124	73 103	—105 136	—52 140	29 22
10		—47 55	—71 77	—10	70 88	27 25	—38 58	13
12		59 65	—25 48	—94 86	39 54	19	—44 30	8
14		42 41	31	26 33	4	49 44	5	—28 30

Table 2. Calculated and observed F-values of hk0 for a Weissenberg photograph
of $(NH_4)_2SbCl_5$. $CuK\alpha$-radiation.

h	h00 F_c F_o	h10 F_c F_o	h20 F_c F_o	h30 F_c F_o	h40 F_c F_o	h50 F_c F_o	h60 F_c F_o	h70 F_c F_o	h80 F_c F_o	h90 F_c F_o
0			26 28		158 183		21 30		108 64	
1		64 64		41 39		56 58		20 14		49 27
2	30 25		— 3 10		24 26		1		18	
3		6 10		8		1 17		9		— 7
4	—28 39		—25 32		—23 26		—19 25		—17	
5		—63 69		—63 57		—47 47		—54 42		—33 22
6	—33 57		—90 81		—28 32		—70 55		—24 17	
7		—32 46		—31 32		—25		—14 10		
8	—62 72		— 7		—54 49		1		—43 27	
9		— 6		5		—16 14		13		
10	12 35			84 86	12 17		72 52			
11		48 54		44 58		38 30				
12	25 17		28 32		27 14					
13		30 27		31 35						

Weissenberg photograph of $(NH_4)_2SbCl_5$. CuKα-radiation.

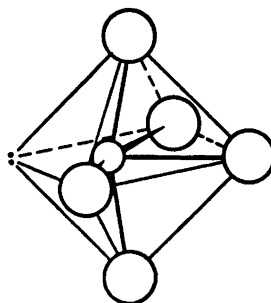| h08		h09		h010		h011		h012		h013		h014		h015	
F_c	F_o	F_c	F_o	F_c	F_o	F_c	F_o	F_c	F_o	F_c	F_o	F_c	F_o	F_c	F_o
—39	36														
30		—34	32												
56	58	—56	52	—25	17	59	20								
52	57	22	20	—82	60	—38	17	26	14	32	17				
71	68	90	82	—14	14	—22	14	—63	40	—14	17				
—90	91	40	44	55	54	11		—1		—26	20	27	28		
—82	63	—21	20	—31	25	30	37	16	14	—58	47	40	28	68	26
7		—21	20	9		12		27	26	—47	36	—79	51	35	26
—18		15		—24	51	—8		97	78	13		—70	37		
37	47	—1		—33	20	—75	66	—2		84	63				
—1	17	30	71	64	48	—75	67	—52	20						
—48	40	—15		62	47										

Fig. 11. The $SbCl_5^{2-}$ group with the assumed stereochemically active unshared electron pair occupying the sixth corner of the octahedron.

The $SbCl_5^{2-}$ group is isotypic with the SbF_5^{2-} group in K_2SbF_5[22], where, however, the Sb—F distance opposite the empty corner seems to be larger than the others. For the similarly five coordinated antimony in the complex $Sb_4F_{16}^{4-}$ in $KSbF_4$[23] this Sb—F distance is the shortest. If we interpret the coordination around one of the antimony atoms in Sb_2S_3[16,17] as a five coordination of this sort we find the Sb—S distance opposite the empty corner to be the shortest. An analogous coordination is also found in TlI[48] around both Tl and I, although we have not isolated complexes here. In this case the distance opposite the empty corner is the shortest.
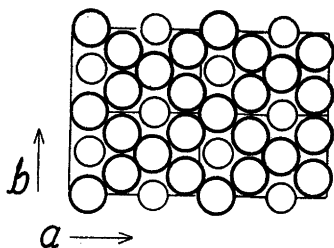
Fig. 12. Approximately close-packed layer at $z \approx 0.36$ projected orthogonally on the ab-plane with four adjacent unit cells. The radii of the circles are equal to the ionic radii of Cl^- (1.81) and NH_4^+ (1.43).
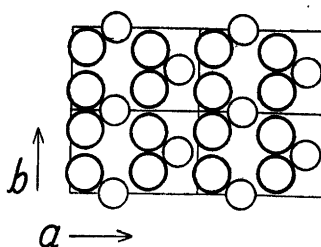
Fig. 13. Approximately close-packed layer with vacant positions at $z \approx 0.12$ projected orthogonally on the ab-plane with four adjacent unit cells. The radii are equal to the ionic radii of Cl^- (1.81) and NH_4^+ (1.43).

We can describe the structure of $(NH_4)_2SbCl_5$ schematically in the following way. The Cl^- and NH_4^+ form together a distorted close-packing with some vacant positions. In this packing we have two types of layers: A, with all positions occupied, see Fig. 12; B, with vacant positions, see Fig. 13. The sequence of the layers is: A,A',B,B',A,A',B,B', ... These layers are approximately parallel with the ab-plane. The Sb atoms are situated in some of the octahedral holes in such a way that one Sb is surrounded by five Cl and with the unshared electron pair directed at the empty position in the close-packing. Orthogonal projections of the structure of $(NH_4)_2SbCl_5$ are given in Fig. 14. The interatomic distances are given in Table 3.
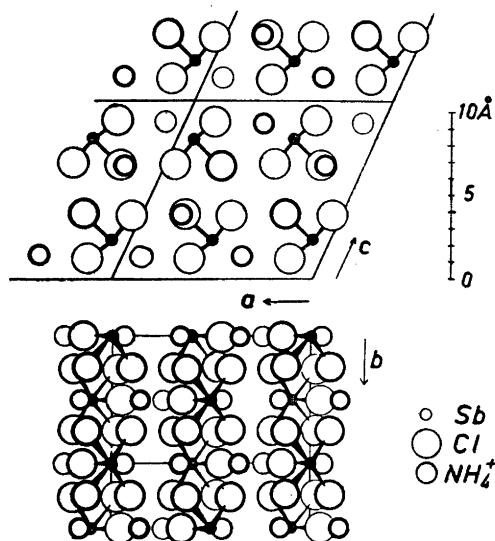

Fig. 14. Orthogonal projections of the structure of $(NH_4)_2SbCl_5$. Parts of adjacent unit cells are given.

Table 3. Interatomic distances in $(NH_4)_2SbCl_5$. *Å units. The numeral 2 × before a distance means that it occurs twice.*

In $SbCl_5^{2-}$ group.

Sb — 5 Cl $2 \times 2.6_2$ $2 \times 2.6_2$ 2.3_6
Cl — Cl 3.7_0 3.7_2 $2 \times 3.6_6$ $2 \times 3.2_9$ $2 \times 3.4_6$

Sb — 4Cl (at the "empty" side of the group) $2 \times 4.3_4$ $2 \times 5.0_6$
$(NH_4^+)_1$—11 Cl $2 \times 3.3_9$ $2 \times 3.5_1$ $2 \times 3.6_1$ $2 \times 3.6_2$ 3.7_7 $2 \times 3.8_6$
$(NH_4^+)_2$—9 Cl $2 \times 3.1_9$ $2 \times 3.3_2$ $2 \times 3.3_8$ 3.6_1 $2 \times 3.8_0$

Cl_1—Sb 2.6_2
Cl_1—4 NH_4^+ 3.1_9 3.3_2 3.3_8 3.3_9
Cl_2—Sb 2.6_2
Cl_2—4 NH_4^+ 3.1_9 3.5_1 3.6_1 3.6_2
Cl_3—Sb 2.3_6
Cl_3—4 NH_4^+ 3.6_1 3.7_7 $2 \times 3.8_6$
Cl_1—7 Cl 3.2_9 3.6_6 3.7_0 3.8_3 4.0_0 4.0_9 4.1_9
Cl_2—8 Cl 3.4_6 3.6_6 3.6_6 3.6_8 3.7_2 3.9_8 4.0_9 4.1_9
Cl_3—8 Cl $2 \times 3.2_9$ $2 \times 3.4_6$ $2 \times 3.6_8$ $2 \times 3.6_8$
$(NH_4^+)_1$—2NH_4^+ 4.4_4 4.4_8
$(NH_4^+)_2$—2NH_4^+ 4.4_4 4.6_0
Sb—Sb 4.8_1
Sb—7 NH_4^+ $2 \times 4.3_4$ 4.3_5 4.4_3 4.5_4 $2 \times 4.5_6$
$(NH_4^+)_1$—4 Sb 4.4_3 4.5_4 $2 \times 4.5_6$
$(NH_4^+)_2$—3 Sb $2 \times 4.3_4$ 4.3_5

The NH_4^+ ions have a fairly irregular coordination with most of the NH_4^+-Cl distances longer than the sum of the ionic radii, which is 3.24 kX[46]. The long distances might perhaps be explained by the fact that NH_4^+ and Cl^- form a sort of close-packing although they have not the same size.

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