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The Crystal Structure of Antimony (III) Sulfobromide, SbSBr*

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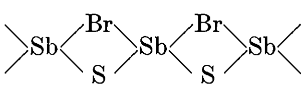
The structure of SbSBr which was reported in approximate form by Dönges (1950) has been refined by means of Fourier syntheses on (001). There are four units of SbSBr in the unit cell for which $a = 8{\cdot}26$, $b = 9{\cdot}79$ and $c = 3{\cdot}97$ Å. The space group is *Pnam* and the atoms all lie in the mirror planes at $z = \frac{1}{4}$ and $z = \frac{3}{4}$. The refinement resulted in shifts of as much as 0·4 Å in the bond distances and suggested a somewhat different interpretation of the bonding than that given by Dönges. The new interpretation is a structure consisting of pleated chains of Sb and S atoms along the c axis with bromine present as Br^- outside the chains. Each Sb has one S atom at 2·49 Å and two S atoms at 2·67 Å. Each S atom is similarly bonded to three Sb atoms. The bond angles around Sb are 84·1° (2) and 96·3° (1) while those around S are 95·9° (2) and 96·3° (1). The nearest neighbors of Br^- are two Sb at 2·94 Å and one S at 3·46 Å.

Introduction

The preparation and approximate structures of a series of compounds of the type *ABX* where *A* is Sb or Bi, *B* is S or Se and *X* is Cl, Br or I were described by Dönges (1950*a*, *b*). Of the twelve possible compounds, all but SbSCl and SbSeCl were prepared. BiSeCl was reported to crystallize with the space-group symmetry *Pmmm* with $z = 12$. The remaining nine compounds were found to crystallize with the space-group symmetry *Pnam* with $z = 4$ and were shown to be isomorphous. In all cases the crystals were needles extended in the c direction. The principal prism faces were of the form {110}, but {100} and {010} were also frequently developed. By the use of some fifteen $hk0$ reflections in each case, Dönges arrived at approximate values for the six atomic positional parameters in several of the compounds. His values for SbSBr are given as Parameter Set No. 1 in Table 2. These values had rather high uncertainties which amounted to approximately 0·1 Å for Sb and Br and approximately 0·4 Å for S. Dönges reported no interatomic distances but proposed a structure consisting of chains of the following type along the c axis:



The Sb–S and Sb–Br separations along the chain, implied by Dönges' parameters, were all approximately 2·9 Å. These chains were said to pair off into double chains due to strong interactions between the Sb atoms of a given chain and the S atoms of another. The implied Sb–S distance here is approximately 2·5 Å. The bonding was assumed by Dönges to be ionic. Where the distances were somewhat less than the sum of the ionic radii, the ions were said to be strongly polarized.

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Because of the unusual nature of the structure proposed for these interesting compounds, a reinvestigation was considered worth while. Antimony sulfobromide was chosen for study since it gave the maximum differences in atomic numbers without going to the more highly absorbing bismuth compounds.

The unit cell and space group

Antimony sulfobromide was prepared by the method of Dönges. Several needles having nearly uniform cross sections about 0·05 mm. in diameter were mounted for the X-ray study. The crystal used for the intensity measurements had a maximum thickness of 0·050 mm. and a minimum thickness of 0·035 mm. The maximum μr for Mo $K\alpha$ radiation was thus 0·6. Since the maximum variation in the absorption correction from $\theta = 0$ to $\theta = 90°$ would have been about 15%, no correction was applied. The lattice constants were determined from a zero level Weissenberg photograph about the c axis and from $h0l$ and $0kl$ precession photographs prepared by use of Mo $K\alpha$ radiation. The Weissenberg film was calibrated by superimposing a powder photograph of pure CeO_2 ($a = 5{\cdot}411 \pm 0{\cdot}001$ Å) on either edge. The lattice constants from the present study are compared with those of Dönges in Table 1.

Table 1. *Lattice constants for* SbSBr *in* (Å)

	a	*b*	*c*
Dönges	8·20	9·70	3·95
Present study	8·26 ± 0·01	9·79 ± 0·02	3·97 ± 0·01

Dönges reported an experimental density of 4·86 g.cm.$^{-3}$. The density calculated on the basis of the new lattice constants and $z = 4$ is 4·84 g.cm.$^{-3}$. Zero and upper level Weissenberg photographs about the c axis and the precession photographs showed only the following systematic absences; $0kl$ with $k+l$ odd, and $h0l$ with h odd. The space groups consistent with these observations are *Pnam* and $Pna2_1$. A comparison of the intensities on the Weissenberg photographs

Table 2. *Positional parameters and R values at various stages of the hk0 Fourier refinement of* SbSBr

		Parameter Set 1	Parameter Set 2	Parameter Set 3	Parameter Set 4	Backshift Corrections	Parameter Set 5
Sb	x	0·120	0·1208	0·1204	0·1203	0·0001	0·1205
	y	0·145	0·1358	0·1331	0·1336	−0·0005	0·1326
Br	x	0·515	0·5116	0·5125	0·5117	0·0008	0·5133
	y	0·835	0·8244	0·8225	0·8223	0·0002	0·8227
S	x	0·825	0·8370	0·8377	0·8378	−0·0001	0·8376
	y	0·080	0·0549	0·0461	0·0466	−0·0005	0·0456
B (Å^2)		1·68	1·09	1·09	—	—	1·09
$R(hk0)$		0·419	0·145	0·101	—	—	0·096

Set 1. Dönges parameters, used as input in Fourier synthesis No. 1.
Set 2. Peak locations in Fourier No. 1; used as input in Fourier No. 2.
Set 3. Peak locations in Fourier No. 2; used as input in Fourier No. 3 (an F_o Fourier) and in Fourier No. 4 (an F_c Fourier). These are also the peak locations on Fourier No. 3.
Set 4. Peak locations on Fourier No. 4 (an F_c Fourier).
Set 5. Parameter Set No. 3 with backshift corrections applied. These are the final parameters.

showed that the ratios $I_{hk0}:I_{hk2}$ were approximately constant as were also those for $I_{hk1}:I_{hk3}$. These observations are consistent with the structure proposed by Dönges in which all atoms are in the mirror planes of *Pnam*.

Zero and first level Weissenberg photographs about the c axis with Mo $K\alpha$ radiation were used for the intensity data. The multiple-film technique was employed with 0·0025 cm. brass foils interleaved between successive films to give a factor of approximately 3·8 from one film to the next. In all, 108 $hk0$ and 94 $hk1$ reflections were observed out of possible totals of 156 and 172 respectively. The intensities were estimated visually and corrected in the usual way to give sets of $|F_o|$ values.

With Dönges' parameters and an estimated isotropic temperature factor of 1·7 Å^2 as a starting point, the structure was refined by means of Fourier syntheses on (001). The progress of the refinement and the final x and y parameters are shown in Table 2. The final Fourier synthesis based on the observed data showed nearly circular peaks of the anticipated relative heights and little false detail. It was next necessary to decide which z parameter ($\frac{1}{4}$ or $\frac{3}{4}$) should be assigned to each atom. One of these may be arbitrarily assigned and Sb was accordingly placed in the mirror at $z = \frac{1}{4}$. Following this assignment, there are four combinations of S and Br positions as shown in Table 3. Because of the ease with which structure

Table 3. *Test of various combinations of z parameters*

	z_{Sb}	z_{Br}	z_S	$R(hkl)$
Case 1	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0·101
Case 2	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$	0·350
Case 3	$\frac{1}{4}$	$\frac{3}{4}$	$\frac{1}{4}$	0·601
Case 4	$\frac{1}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	0·629

factor calculations could be made on SWAC, sets of $F(hkl)$ values and corresponding R values were calculated for each combination. The results shown in Table 3 clearly indicate that the first combination (the one proposed by Dönges) with all atoms at $z = \frac{1}{4}$ is correct. The F_c values calculated on the basis

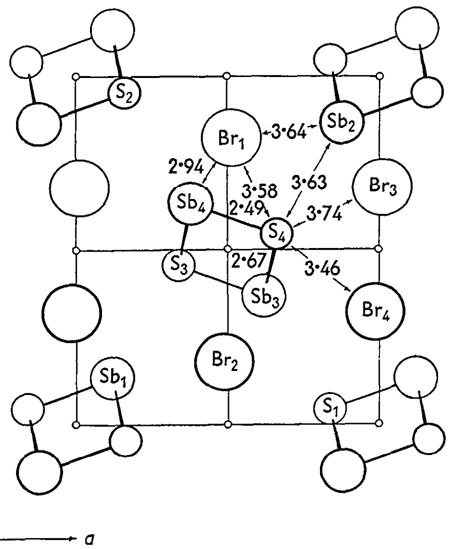

Fig. 1. Projection of the structure of SbSBr on (001). Distances are indicated in Å.

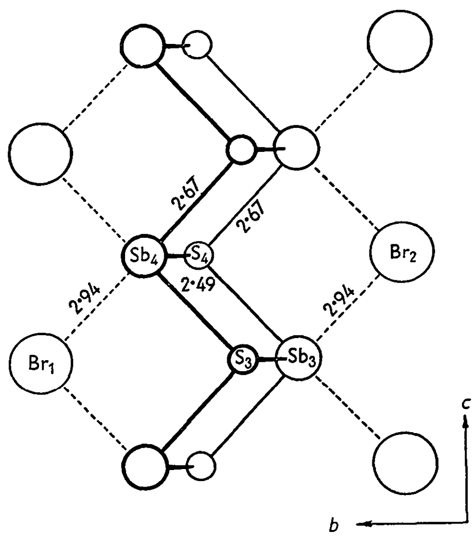

Fig. 2. Projection of the structure of SbSBr on (100). Distances are indicated in Å.

Table 4. *Comparison of observed and calculaled structure factors for* SbSBr

h	k	l	F_o	F_c
00	02	00	50	49-
00	04	00	115	160-
00	06	00	94	104
00	08	00	<15	19
00	10	00	48	48-
00	12	00	34	40-
00	14	00	<23	7-
00	16	00	<24	36
01	02	00	93	107-
01	03	00	37	26
01	04	00	60	58
01	05	00	105	116-
01	06	00	92	105
01	07	00	57	60
01	08	00	<15	11-
01	09	00	63	57
01	10	00	36	39-
01	11	00	92	99-
01	12	00	<20	17
01	13	00	<21	1-
01	14	00	<23	18
01	15	00	34	41
02	00	00	101	106
02	01	00	94	100-
02	02	00	91	85-
02	03	00	70	68-
02	04	00	44	38-
02	05	00	115	132
02	06	00	81	73
02	07	00	79	79
02	08	00	44	39-
02	09	00	71	74-
02	10	00	<18	13
02	11	00	<27	20-
02	12	00	35	30
02	13	00	44	51
02	14	00	<23	23-
03	01	00	134	153-
03	02	00	118	134-
03	03	00	124	138
03	04	00	51	42
03	05	00	21	21-
03	06	00	75	76
03	07	00	49	50-
03	08	00	32	31-
03	09	00	45	41
03	10	00	34	38-
03	11	00	<19	19
03	12	00	<21	17
03	13	00	26	26
03	14	00	<23	25
04	00	00	83	75-
04	01	00	<11	7
04	02	00	63	56-
04	03	00	38	35-
04	04	00	94	92
04	05	00	31	28-
04	06	00	42	30
04	07	00	<16	6
04	08	00	111	114-
04	09	00	31	26-
04	10	00	44	47
04	11	00	<20	6-
04	12	00	80	76
04	13	00	<23	20
04	14	00	37	47-

h	k	l	F_o	F_c
05	01	00	91	87-
05	02	00	39	31
05	03	00	137	147
05	04	00	<14	9-
05	05	00	<21	1-
05	06	00	91	86-
05	07	00	75	68-
05	08	00	<25	7-
05	09	00	<26	8
05	10	00	54	46
05	11	00	<21	7
05	12	00	<22	23-
06	00	00	78	71
06	01	00	107	107
06	02	00	<14	12-
06	03	00	57	50
06	04	00	<15	13
06	05	00	92	98-
06	06	00	33	36
06	07	00	<18	13-
06	08	00	55	58-
06	09	00	38	48
06	10	00	<20	5-
06	14	00	34	30-
07	01	00	36	28
07	02	00	68	61
07	03	00	22	17
07	04	00	34	31
07	05	00	62	54-
07	06	00	60	56-
07	07	00	25	28
07	08	00	28	19
07	09	00	34	29
07	10	00	56	62
07	11	00	62	58-
07	12	00	35	33-
07	13	00	<34	2-
08	00	00	116	116
08	01	00	51	49
08	02	00	35	38-
08	03	00	22	19
08	04	00	91	85-
08	05	00	<18	15-
08	06	00	50	50
08	07	00	39	32
08	08	00	29	31
09	01	00	<18	10
09	02	00	57	57-
09	03	00	32	28-
09	04	00	32	38
09	05	00	44	53-
09	06	00	20	23
09	07	00	44	48
09	08	00	<22	18-
09	09	00	44	42
09	10	00	<23	1-
09	11	00	33	41-
10	00	00	28	33
10	01	00	23	21-
10	02	00	28	27-
10	03	00	52	48-
10	04	00	27	26-
10	05	00	<29	19
10	06	00	28	26
10	07	00	35	35
10	08	00	<23	1

h	k	l	F_o	F_c
10	09	00	49	52-
11	01	00	21	23-
11	02	00	70	75-
11	03	00	39	40
11	04	00	<31	21
11	05	00	<23	2-
11	06	00	<23	19
11	07	00	<23	19-
11	08	00	32	30-
12	00	00	<23	17-
12	01	00	<23	9
12	02	00	<23	4
12	03	00	<23	16-
12	04	00	40	40
12	05	00	<23	5-
12	06	00	<34	0
12	07	00	<24	22
12	08	00	42	45-
13	01	00	<24	22-
13	02	00	<24	2
13	03	00	39	42
13	07	00	33	29-
14	00	00	<25	6-
14	01	00	35	41
00	03	01	116	145-
00	05	01	18	23
00	07	01	87	87
00	09	01	109	121-
00	11	01	32	30-
00	13	01	81	90
01	02	01	153	216-
01	03	01	90	98
01	04	01	90	90
01	05	01	57	55
01	06	01	36	36
01	07	01	73	73-
01	08	01	69	64-
01	09	01	46	39-
01	10	01	<18	4-
01	11	01	25	33
01	12	01	<20	1-
01	13	01	<22	4-
01	14	01	23	28
02	00	01	124	141-
02	01	01	96	92
02	02	01	62	55
02	03	01	<10	11-
02	04	01	127	148
02	05	01	38	31-
02	06	01	49	46-
02	07	01	78	76
02	08	01	84	89-
02	09	01	32	28-
02	10	01	<18	16
02	11	01	<19	14-
02	12	01	23	32
02	13	01	28	29
02	14	01	<23	30-
03	01	01	67	62-
03	02	01	47	40
03	03	01	64	63
03	04	01	95	90
03	05	01	62	60
03	06	01	67	63-
03	07	01	70	65-
03	08	01	<16	12

h	k	l	F_o	F_c
03	09	01	28	32-
03	10	01	92	88
03	11	01	50	55
03	12	01	45	48-
03	13	01	<22	3
03	14	01	35	33-
03	15	01	<34	32-
04	00	01	78	71-
04	01	01	151	174
04	02	01	<17	4-
04	03	01	79	72
04	04	01	<13	9
04	05	01	117	115-
04	06	01	27	19-
04	07	01	33	28
04	08	01	26	18
04	09	01	45	50
04	10	01	<19	15
04	11	01	<20	4
04	12	01	<21	8
04	13	01	<31	24-
04	14	01	<23	11
04	15	01	<34	25-
05	01	01	40	33
05	02	01	34	31
05	03	01	98	97-
05	04	01	36	33
05	05	01	21	14-
05	06	01	98	98-
05	07	01	54	55
05	08	01	<18	5-
05	09	01	23	14
05	10	01	76	78
05	11	01	<21	6-
05	12	01	38	41-
05	13	01	<23	0
05	14	01	<23	24-
06	00	01	75	65
06	01	01	65	57
06	02	01	<14	6
06	03	01	28	20-
06	04	01	89	84-
06	05	01	76	67-
06	06	01	<17	0
06	07	01	28	19
06	08	01	91	84
06	09	01	<19	18-
06	10	01	<28	27-
06	11	01	<30	6-
06	12	01	39	47-
06	13	01	<23	20
06	14	01	<34	34
07	01	01	87	82
07	02	01	101	94-
07	03	01	79	76-
07	04	01	34	38
07	05	01	<18	11-
07	06	01	<25	12
07	07	01	43	47
07	08	01	33	37-
07	09	01	<28	9-
07	10	01	<21	1-
07	11	01	28	31-
07	12	01	<23	1-
07	13	01	<24	15-
07	14	01	<25	17

h	k	l	F_o	F_c
08	00	01	<24	6
08	01	01	23	20-
08	02	01	36	33
08	03	01	48	47-
08	04	01	<18	1-
08	05	01	40	41
08	06	01	22	22-
08	07	01	61	61
08	08	01	<21	22
08	09	01	54	60-
08	10	01	<31	18-
08	11	01	<33	17-
08	12	01	<34	26-
08	13	01	35	47
08	14	01	<25	11
09	01	01	<18	6-
09	02	01	74	75-
09	03	01	<19	2
09	04	01	54	54
09	05	01	41	37
09	06	01	55	52
09	07	01	<29	25-
09	08	01	<31	18-
09	09	01	34	27-
09	10	01	<23	11-
09	11	01	<34	32
09	12	01	<24	3
09	13	01	<25	3-
09	14	01	<26	13
10	00	01	104	97-
10	01	01	<28	14
10	02	01	<20	14
10	03	01	<20	7-
10	04	01	57	56
10	05	01	<21	7
10	06	01	28	34-
10	07	01	<31	33
10	08	01	<23	17-
10	09	01	<23	17-
10	10	01	<34	20
10	11	01	<25	7-
10	12	01	<36	20
11	01	01	37	32-
11	02	01	<22	6
11	03	01	<22	3
11	04	01	<22	11
11	05	01	31	37
11	06	01	<33	28-
11	07	01	<23	28-
11	08	01	<24	2-
11	09	01	<24	19-
11	10	01	<25	25
11	11	01	39	46
12	00	01	37	42-
12	01	01	36	41
12	02	01	<23	13
12	03	01	<33	14
12	04	01	<23	18
12	05	01	54	50-
13	01	01	<34	25
13	02	01	<34	22
13	03	01	<24	28-
13	04	01	<24	2-
13	05	01	<35	8
13	06	01	38	38-

of the final parameters are compared with the F_o values in Table 4.

Discussion of the structure

Projections of the structure as a whole on the (001) plane and of one of the chains on the (100) plane are shown in Figs. 1 and 2 respectively. The shifts in atomic parameters resulting from the refinement indicate a somewhat different bonding arrangement than that reported by Dönges. There is even stronger indication of a chain structure along the *c* axis but it is suggested that these consist of essentially covalently bonded Sb and S atoms with bromine atoms standing out from the chains at distances which imply that they are bromide ions. The Sb–S bond distances of 2·49 Å and 2·67 Å are in the range of values (2·38 Å to 2·67 Å for the three nearest neighbors of each Sb) reported by Hofmann (1933) in Sb_2S_3. In fact the chains in the two structures are quite similar if one removes one sulfur atom from each unit of the chain in Sb_2S_3 and adds two bromide ions to the positions in which these are found in SbSBr. Similarities in the two structures were noted by Dönges but the refined structure for SbSBr shows these even more strikingly.

Table 5. *Interatomic distances and bond angles in* SbSBr

Distances (Å) $\sigma \sim 0·02$ Å

Sb_3–S_3	2·49	S_4–Br_4	3·46
Sb_3–S_4	2·67	S_4–Br_1	3·58
Sb_3–S_1	3·63	S_4–Br_3	3·74
Sb_3–Br_2	2·94	S_4–Br_2	3·89
Sb_3–Br_4	3·64	S_4–S_3	3·46
Sb_3–Sb_4	3·83	Br_3–Br_4	4·01

Angles (degrees) $\sigma \sim 1·0°$

Sb_3–S_4–Sb_4	95·9	S_4–Sb_3–S_3	84·1
Sb_3–S_4–Sb_3	96·3	S_4–Sb_3–S_4	96·3

The observed interatomic distances and bond angles for the refined structure are given in Table 5.

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