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A Redetermination of the Structure of Miargyrite, $AgSbS_2$

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The crystal structure of miargyrite ($8AgSbS_2$, Cc, $a=12{\cdot}862$, $b=4{\cdot}411$, $c=13{\cdot}220$ Å $\pm 0{\cdot}1\%$, $\beta=98°38'\pm0{\cdot}5'$) was determined by three-dimensional least-squares techniques. The Ag and Sb atoms lie near the alternate positions of the Pb atoms in galena, but the S atoms are displaced greatly from those in galena resulting in a threefold coordination for the two Sb atoms (2·58, 2·58, and 2·53 Å for one and 2·48, 2·49, and 2·54 Å for the other), twofold for one of the Ag atoms (2·36 and 2·46 Å) and threefold for the other (2·44, 2·50, and 2·58 Å). The coordination of the Sb atoms is closely similar to those in livingstonite ($HgSb_4S_8$), jamesonite ($Pb_4FeSb_6S_{14}$), stibnite (Sb_2S_3), pyrargyrite (Ag_3SbS_3), freieslebenite ($PbAgSbS_3$), and wolfsbergite ($CuSbS_2$). The coordinations of the Ag atoms are similar to those in pyrargyrite (Ag_3SbS_3), proustite (Ag_3AsS_3), stromeyerite ($AgCuS$) and freieslebenite ($PbAgSbS_3$).

Introduction

Hofmann (1938) examined miargyrite ($AgSbS_2$) by Weissenberg techniques, and was able to propose a structure (Table 1) by first locating the heavy atoms from the patterns of strong reflections and then postulating the positions of the sulfur atoms from packing considerations. No intensity measurements were made, and although the general nature of a structure can be determined in this manner the actual details concerning the S atoms are obscured by the dominant scattering of the heavy atoms. Graham (1951) showed that the structures of miargyrite ($AgSbS_2$), matildite ($AgBiS_2$) and aramayoite ($Ag(Sb,Bi)S_2$) were based on the galena structure with the heavy atoms occupying the Pb position in galena. Hellner (1958) has classified these, and other sulfides, on the basis of their resemblance in structure to galena.

Table 1. *Atomic coordinates obtained from Hofmann*

Atom	x	y	z
S(1)	0	0	0
S(2)	0	0·50	¼
S(3)	0·25	0·00	0·375
Sb	0·125	0·50	0·44
Ag	0·125	0·00	0·19

The present investigation was carried out to test the structure proposed for miargyrite by Hofmann, and to determine accurately the coordination.

Experimental

The sample of miargyrite, from Bräunsdorf, Saxony, was kindly supplied by the Mineralogical Museum of the University of Toronto (number R569).

The cell dimensions of miargyrite, determined on a powder diffractometer using spinel as an internal standard are:

$$a=12{\cdot}862\pm0{\cdot}013,\ b=4{\cdot}411\pm0{\cdot}004,$$
$$c=13{\cdot}220\pm0{\cdot}010\ \text{Å};\ \beta=98°\ 38'\pm0{\cdot}5',$$

which agree quite closely with those given by Hofmann. The spinel was itself calibrated with spectroscopically pure silicon ($a=8{\cdot}080$ Å). A copy of the indexed powder pattern has been submitted to the Powder Diffraction Data File. The systematic extinctions yield the space group $C2/c$ or Cc.

The intensities were measured on a single-crystal diffractometer with Weissenberg type geometry, a scintillation counter and monochromatized Mo $K\alpha$ radiation being used. Because of the high absorption, a crystal was ground to a sphere of 0·11 mm radius in order to apply corrections more easily and accurately. The intensities were corrected for Lorentz-polarization factors, and for absorption with the use of Van den Hende's (1963) approximation:

$$(E+F\sin^2\theta+G\sin^4\theta+H\sin^6\theta)\ .$$

E, F, G, and H were determined from the absorption correction factors for spheres in *International Tables for X-ray Crystallography* (1959) and the corrections were made with a program written for the IBM 1620 computer by Dr. G. V. Gibbs and the author.

The $F^2(h0l)$ values were run on the analog computer XRAC (by permission of Prof. R. Pepinsky) to obtain the b-axis Patterson projection. This Patterson map was interpreted, with the use of implication diagrams, as having a metal atom at the origin in contrast to the structure of Hofmann with a sulfur atom at the origin.

Structure-factor calculations were made with an IBM 1620 computer program written by Professor W. Macintyre of the University of Colorado. This program utilizes the approximation of Vand, Eiland &

Table 2. *Observed and calculated structure amplitudes*

h	k	l	F_o	F_c
2	0	0	82	-82
4	0	0	212	210
6	0	0	9	-13
8	0	0	291	269
10	0	0	22	-13
12	0	0	137	135
14	0	0	9	-10
16	0	0	95	96
18	0	0	8	-12
0	0	2	25	-25
2	0	2	50	51
4	0	2	9	19
6	0	2	16	-18
8	0	2	91	-80
10	0	2	74	74
12	0	2	20	-20
14	0	2	11	-15
16	0	2	57	-62
18	0	2	46	47
0	0	4	30	-44
2	0	4	385	376
4	0	4	20	-25
6	0	4	199	192
8	0	4	19	-24
10	0	4	175	171
12	0	4	16	-23
14	0	4	103	119
16	0	4	11	-8
18	0	4	47	51
0	0	6	22	-11
2	0	6	67	-71
4	0	6	60	60
6	0	6	2	16
8	0	6	14	-13
10	0	6	83	-85
12	0	6	58	55
14	0	6	27	-21
16	0	6	4	15
0	0	8	181	183
2	0	8	40	-48
4	0	8	220	219
6	0	8	30	-36
8	0	8	147	154
10	0	8	20	-21
12	0	8	88	89
14	0	8	17	-28
16	0	8	84	89
0	0	10	29	29
2	0	10	14	-1
4	0	10	74	-82
6	0	10	47	48
8	0	10	8	7
10	0	10	3	12
12	0	10	67	-64
14	0	10	32	31
0	0	12	36	37
2	0	12	135	144
4	0	12	33	-37
6	0	12	123	116
8	0	12	38	-40
10	0	12	106	112
12	0	12	15	13
0	0	14	27	30
2	0	14	16	17
4	0	14	3	10
6	0	14	65	-65
8	0	14	34	29
10	0	14	28	-16
0	0	16	108	107
2	0	16	45	42
4	0	16	100	105
6	0	16	23	22
8	0	16	52	57
0	0	18	43	-46
2	0	18	23	21
1	1	0	9	-8
3	1	0	40	36
5	1	0	40	-37
7	1	0	19	21
9	1	0	14	-24
11	1	0	61	57
13	1	0	54	-51
15	1	0	31	27
17	1	0	11	-20
1	1	1	7	14
3	1	1	45	46
5	1	1	53	-38
7	1	1	3	14
9	1	1	40	-28
11	1	1	3	8
13	1	1	7	16
15	1	1	3	13
17	1	1	31	-27
1	1	2	245	-243
3	1	2	15	15
5	1	2	279	-283
7	1	2	28	17
9	1	2	167	-167
11	1	2	9	10
13	1	2	118	-124
15	1	2	15	13
17	1	2	78	-86
1	1	3	32	-43
3	1	3	15	-17
5	1	3	92	92
7	1	3	39	-48
9	1	3	16	-18
11	1	3	3	-17
13	1	3	44	41
15	1	3	20	-22
1	1	4	7	-5
3	1	4	2	-12
5	1	4	60	59
7	1	4	44	-47
9	1	4	24	23
11	1	4	4	-20
13	1	4	65	57
15	1	4	35	-40
17	1	4	30	29
1	1	5	2	14
3	1	5	34	-28
5	1	5	2	14
7	1	5	5	13
9	1	5	6	20
11	1	5	46	-37
13	1	5	13	-11
15	1	5	16	20
17	1	5	4	13
1	1	6	27	-32
3	1	6	201	-203
5	1	6	22	28
7	1	6	186	-186
9	1	6	30	27
11	1	6	126	-129
13	1	6	11	13
15	1	6	70	-75
17	1	6	6	16
1	1	7	24	-39
3	1	7	28	-29
5	1	7	2	-25
7	1	7	70	61
9	1	7	23	-28
11	1	7	3	3
13	1	7	4	-20
15	1	7	17	17
1	1	8	23	-28
3	1	8	2	2
5	1	8	13	-13
7	1	8	65	63
11	1	8	27	26
13	1	8	11	-18
1	1	9	13	-14
3	1	9	15	23
5	1	9	47	-37
7	1	9	12	-12
9	1	9	16	18
11	1	9	11	22
15	1	9	6	-14
1	1	10	178	-191
3	1	10	40	-39
5	1	10	161	-146
7	1	10	22	27
9	1	10	99	-108
11	1	10	24	29
13	1	10	92	-89
1	1	11	66	63
3	1	11	15	-23
5	1	11	6	-11
7	1	11	3	-25
9	1	11	28	27
11	1	11	11	-16
13	1	11	15	14
1	1	12	37	45
3	1	12	23	-28
5	1	12	10	9
7	1	12	5	-15
9	1	12	53	50
11	1	12	22	-26
13	1	12	26	28
1	1	13	7	[illegible]
3	1	13	7	10
5	1	13	21	27
7	1	13	34	-29
9	1	13	15	-18
11	1	13	15	13
1	1	14	32	-36
3	1	14	120	-114
5	1	14	40	-39
7	1	14	103	-99
9	1	14	21	-21
1	1	15	5	-25
3	1	15	35	31
5	1	15	10	-14
7	1	15	10	10
9	1	15	4	-18
1	1	16	4	-13
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5	1	16	23	-21
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1	1	18	76	-82
3	1	18	30	-25
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4	2	0	252	250
6	2	0	18	10
8	2	0	180	154
10	2	0	22	-4
12	2	0	132	128
14	2	0	5	7
16	2	0	88	81
18	2	0	8	-4
0	2	1	115	-111
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4	2	1	11	17
6	2	1	8	38
8	2	1	97	-96
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12	2	1	12	-7
14	2	1	7	29
16	2	1	37	-42
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4	2	2	28	-28
6	2	2	46	42
8	2	2	31	-27
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12	2	2	49	-48
14	2	2	36	38
16	2	2	24	-24
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0	2	3	61	-65
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6	2	3	54	45
8	2	3	10	-17
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12	2	3	5	-22
14	2	3	39	37
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4	2	4	33	-24
6	2	4	195	187
8	2	4	15	17
10	2	4	123	128
12	2	4	23	-10
14	2	4	81	83
16	2	4	4	-12
18	2	4	53	63
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2	2	5	105	-110
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6	2	5	12	11
8	2	5	9	41
10	2	5	69	-68
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14	2	5	20	-17
16	2	5	8	30
0	2	6	24	24
2	2	6	5	-12
4	2	6	4	-2
6	2	6	47	-48
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10	2	6	25	-22
12	2	6	9	13
14	2	6	43	-45
16	2	6	23	24
0	2	7	39	41
2	2	7	3	-29
4	2	7	31	24
6	2	7	34	-34
8	2	7	55	47
10	2	7	15	11
12	2	7	10	-15
14	2	7	5	-19
16	2	7	28	25
0	2	8	181	189
2	2	8	25	25
4	2	8	153	151
6	2	8	34	-29
8	2	8	112	117
10	2	8	16	22
12	2	8	86	95
14	2	8	15	-10
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2	2	9	9	48
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6	2	11	5	-9
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0	2	12	42	41
2	2	12	117	120
4	2	12	28	28
6	2	12	104	108
8	2	12	30	23
10	2	12	65	66
12	2	12	15	22
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6	2	13	45	-44
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6	2	14	11	-12
8	2	14	9	12
10	2	14	40	-35
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2	2	15	28	-31
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6	2	15	11	16
8	2	15	6	-9
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4	2	16	59	69
6	2	16	24	27
0	2	17	42	-41
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-4	0	2	6	-12
-6	0	2	57	-46
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-12	0	2	8	-18
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-16	0	10	10	-14
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-7	1	10	187	-186
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-11	1	10	119	-108
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-15	1	10	100	-104
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-13	1	14	94	-99
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-3	1	15	5	-13
-5	1	15	56	46
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-13	1	15	36	26
-1	1	16	7	8
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-5	1	16	14	18
-7	1	16	4	12
-9	1	16	24	22
-11	1	16	9	12
-1	1	17	21	23
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-5	1	17	4	4
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-9	1	17	10	7
-1	1	18	37	-37
-3	1	18	85	-88
-5	1	18	38	-35
-7	1	18	69	-74
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-4	2	1	34	-30
-6	2	1	5	41
-8	2	1	51	-37
-10	2	1	3	24
-12	2	1	48	-36
-14	2	1	14	10
-16	2	1	4	11
-18	2	1	4	11
-2	2	2	3	5
-4	2	2	31	29
-6	2	2	29	-29
-8	2	2	18	6
-10	2	2	36	-37
-12	2	2	43	46
-14	2	2	29	-25
-16	2	2	15	15
-18	2	2	29	-35
-2	2	3	22	26
-4	2	3	33	-32
-6	2	3	105	97
-8	2	3	61	-76
-10	2	3	11	-9
-12	2	3	6	-24
-14	2	3	55	60
-16	2	3	37	-44
-18	2	3	6	10
-2	2	4	254	250
-4	2	4	28	23
-6	2	4	168	164
-8	2	4	19	7
-10	2	4	168	163
-12	2	4	14	8
-14	2	4	95	92
-16	2	4	13	-6
-18	2	4	61	68
-2	2	5	12	-23
-4	2	5	50	54
-6	2	5	70	-72
-8	2	5	2	29
-10	2	5	28	-24
-12	2	5	9	20
-14	2	5	20	-12
-16	2	5	4	12
-18	2	5	26	-23
-2	2	6	5	-14
-4	2	6	21	-23
-6	2	6	14	6
-8	2	6	13	-21
-10	2	6	43	39
-12	2	6	26	-25
-14	2	6	18	13
-16	2	6	23	-31
-2	2	7	22	-30
-4	2	7	69	67
-6	2	7	48	-63
-8	2	7	4	17
-10	2	7	7	-19
-12	2	7	54	62
-14	2	7	56	-53
-16	2	7	4	8
-2	2	8	45	39
-4	2	8	151	151
-6	2	8	23	17
-8	2	8	173	165
-10	2	8	28	26
-12	2	8	103	94
-14	2	8	15	9
-16	2	8	89	85
-2	2	9	45	48
-4	2	9	94	-84
-6	2	9	5	37
-8	2	9	8	-19
-10	2	9	3	25
-12	2	9	46	-34
-14	2	9	3	15
-16	2	9	16	-17
-2	2	10	13	-14
-4	2	10	17	9
-6	2	10	7	17
-8	2	10	18	-21
-10	2	10	20	-20
-12	2	10	21	14
-14	2	10	13	-22
-16	2	10	30	32
-2	2	11	33	32
-4	2	11	24	-34
-6	2	11	19	28
-8	2	11	18	-17
-10	2	11	50	47
-12	2	11	48	-48
-16	2	11	6	-13
-2	2	12	118	124
-4	2	12	18	22
-6	2	12	133	133
-8	2	12	39	38
-10	2	12	99	88
-12	2	12	16	13
-14	2	12	102	88
-2	2	13	81	-67
-4	2	13	38	40
-6	2	13	3	-17
-8	2	13	3	24
-10	2	13	54	-47
-12	2	13	5	22
-14	2	13	6	-12
-2	2	14	10	7
-4	2	14	12	16
-6	2	14	7	-12
-8	2	14	13	-14
-10	2	14	18	16
-12	2	14	4	-15
-2	2	15	3	-11
-4	2	15	26	30
-6	2	15	24	-20
-8	2	15	22	27
-10	2	15	28	-30
-12	2	15	4	18
-2	2	16	29	25
-4	2	16	88	90
-6	2	16	37	38
-8	2	16	70	76
-10	2	16	20	15
-12	2	16	79	74
-2	2	17	33	35
-4	2	17	4	-7
-6	2	17	4	19
-8	2	17	45	-42
-2	2	18	4	13
-4	2	18	9	-16

Table 3. *Final atomic coordinates*

Atom	x	y	z	B
Ag(1)	0·0000	0·0000	0·2500	1·16 ± 0·06
Ag(2)	0·0091 ± 0·0004	0·5173 ± 0·0023	0·4996 ± 0·0004	1·21 ± 0·06
Sb(1)	0·2585 ± 0·0002	0·9568 ± 0·0016	0·6207 ± 0·0002	0·95 ± 0·06
Sb(2)	0·7486 ± 0·0004	0·0526 ± 0·0017	0·3652 ± 0·0004	0·92 ± 0·06
S(1)	0·1457 ± 0·0008	0·3754 ± 0·0046	0·6875 ± 0·0010	1·52 ± 0·22
S(2)	0·8612 ± 0·0009	0·6709 ± 0·0052	0·2941 ± 0·0011	0·90 ± 0·16
S(3)	0·1161 ± 0·0008	0·1815 ± 0·0046	0·4072 ± 0·0008	1·72 ± 0·19
S(4)	0·8966 ± 0·0010	0·8399 ± 0·0055	0·5757 ± 0·0010	0·40 ± 0·14

Pepinsky (1957) for the atomic form factors which were derived from the Thomas–Fermi atomic scattering factor curves. The following constants of the approximation were used:

	A	a	B	b
Ag	31·09	2·063	15·91	40·48
Sb	34·03	2·009	16·97	39·21
S	9·47	2·890	6·53	62·60

Calculations made for the $h0l$ reflections on the basis of the new metal positions determined from the Patterson projection and the sulfur atoms placed in the octahedral hole formed by these metal atoms resulted in an R value of 31%. An electron-density projection was then made by applying the signs of the calculated structure factors to the F_o values. A two-dimensional refinement was carried out with (F_o-F_c) syntheses, and better agreement was obtained showing only minor shifts of the atomic positions in the $(x0z)$-plane.

Generalized projections were then made, by the method described by Fridrichsons & Mathieson (1955) to determine the y coordinates. The sulfur atom showed a marked change along the b direction from the position postulated by Hofmann. The metal atoms showed a shift in the b direction, which was only minor in comparison.

Least-squares calculations were made by means of the Busing–Levy (ORFLS) least-squares program on the IBM 7090 computer. Scattering curves were taken from *International Tables for X-ray Crystallography* (1962).

The R value was still very high (0·27) after several cycles of least-squares refinement using three-dimensional data and assuming the space group $C2/c$. Similar high R values been obtained previously for structures with hypersymmetry in which a mere shift of origin was sufficient to permit a large reduction of the discrepancy index (Marsh, Pauling & McCullough, 1953). Since miargyrite has a grid structure, it was found essentially the same structure was formed if a shift of $c/4$ was made, using a $C2/c$ space group. Least-squares refinement after the shift, and assuming a Cc space group, gave $R=0{\cdot}13$ for 766 reflections and $R=0{\cdot}08$ excluding the 83 unobserved reflections. Miargyrite has a superstructure resulting in weak intensities for half of the reflections: these give $R=0{\cdot}31$ compared with $R=0{\cdot}04$ for the main reflections. The calculated structure amplitudes are given in Table 2.

Examination of the atomic coordinates shows that they deviate by many times the error from values required for a centrosymmetric structure; consequently, the space group of miargyrite may be taken to be Cc.

By X-ray analysis it is difficult to distinguish Ag from Sb because of their similar scattering abilities (Ag with 47 electrons and Sb with 51). In order to differentiate these two atoms, least-squares calculations were made, keeping the atomic positions of Table 3 constant, applying a temperature factor of 1·0 to both Ag and Sb, and permitting this value to vary. The positions of the Ag and Sb were then interchanged using the same input as before. The result was a change in temperature factor to compensate for the change in scattering matter. The temperature factors for the S atoms remained within the standard error but the metal atoms showed a change larger than the error. In one set of calculations the temperature factors for the two Ag atoms were 1·21 and 1·15, and for the Sb atom 0·95 and 0·92, all ± 0·06. In the other set, the values were 1·5 and 1·5 for Ag and 0·5 and 0·8 for Sb, all ± 0·09. Because similar temperature factors would be expected for both Ag and Sb it may be concluded that the former assignment of atoms is correct. This pattern of atoms is confirmed by the observed coordination as is shown in the next section.

Discussion of the structure

The structure of miargyrite projected along the y axis is shown in Fig. 1. The interatomic distances calculated from the coordinates given in Table 3 are listed in Table 4. The average standard deviation of the Ag–S and Sb–S bond lengths is 0·015 Å and that of the S–S distances is 0·02 Å.

The heavy atoms form a framework which is indeed related to the galena structure. Although these heavy atoms are displaced only slightly from the corresponding lead atoms in galena, the sulfur atoms are displaced to such a degree that it is hard to see the resemblance to the galena structure. In Table 4 the bond distances are given for the six nearest neighbors of the two types of heavy atoms to illustrate the relation to the octahedral coordination of the metal atom in galena.

Each of the antimony atoms exhibits threefold coordination with Sb situated at one vertex of a trigonal pyramid and three S atoms forming the base at dis-

Table 4. *Interatomic distances*

Ag(1)–S(2)	2·44 Å	Sb(2)–S(3)	2·48 Å
–S(3)	2·50	–S(2)	2·49
–S(4)	2·58	–S(1)	2·54
–S(1)	2·72	–S(4)	3·26
–S(1*a*)	3·50	–S(2*a*)	3·29
–S(2*a*)	3·55	–S(3*a*)	3·34
Ag(2)–S(4)	2·36	Ag(1)–Ag(2)	4·00
–S(3)	2·46	–Sb(1)	3·89
–S(1)	2·89	–Sb(2)	3·87
–S(2)	3·15	Ag(2)–Sb(1)	3·88
–S(3*a*)	3·53	–Sb(2)	3·78
–S(4*a*)	3·53	Sb(1)–Sb(2)	3·80
Sb(1)–S(2)	2·53	S(1)–S(2)	3·53
–S(1)	2·58	–S(3)	3·77
–S(4)	2·58	–S(4)	3·90
–S(1*a*)	3·14	S(2)–S(3)	4·02
–S(3)	3·28	–S(4)	3·74
–S(4*a*)	3·25	S(3)–S(4)	4·01

The S atom, written subscript *a*, signifies a shift of $y+1$. This shift is necessary to show the six nearest neighbors.

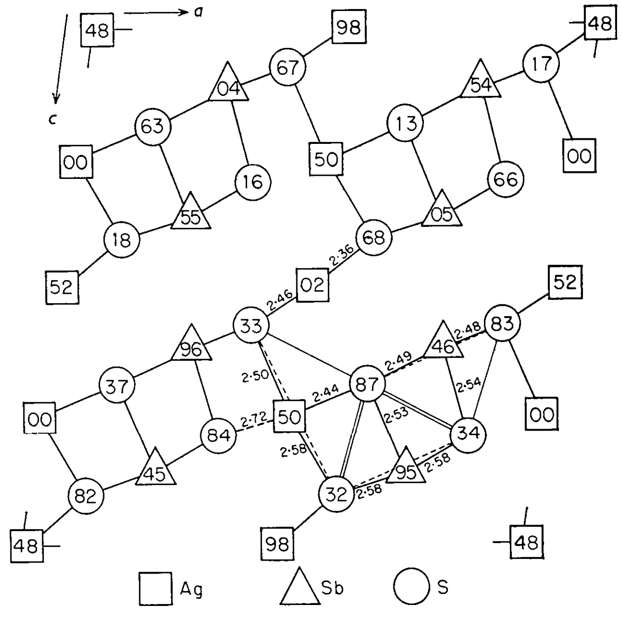

Fig. 1. Projection down the *b* axis showing the shortest metal–sulfur bond distances as indicated by the heavy lines. The trigonal pyramid of the Sb atoms and the distorted pyramid of Ag(1) have the triangular base of the pyramid outlined by light lines with a double line indicating a shared edge. The Ag(2) atom shows only two short bonds. The heights along the *b* axis of the atoms are shown as percentages of the repeat unit.

tances of 2·48 Å to 2·58 Å. These pyramids are bonded together by sharing two sulfur atoms, and the coupled pyramids are joined to one another by the Ag(2) atoms, again in pyramidal coordination, to form chains running diagonally through the unit cell parallel to the [101] direction. The se diagonal chains are connected to each other by the Ag(1) atom as shown in Fig. 1.

This threefold coordination of antimony is seen in several other sulfides: livingstonite, $HgSb_4S_6$, and jamesonite, $FePb_4Sb_6S_{14}$ (Niizeki & Buerger, 1957*a*,*b*); stibnite, Sb_2S_3 (Scavnicar, 1960); pyrargyrite, Ag_3SbS_3 (Harker, 1936); freieslebenite, $PbAgSbS_3$ (Hellner, 1957); and wolfsbergite, $CuSbS_2$ (Hofmann, 1933). The silver atoms, however, show two types of coordination. Ag(1) has threefold coordination with three short bonds (2·44 Å, 2·50 Å and 2·58 Å); whereas Ag(2) has only two short bonds (2·36 and 2·46 Å). Both types of Ag–S coordination are seen in the structure of proustite, Ag_3AsS_3, and pyrargyrite, Ag_3SbS_3 (Harker, 1936) and similar bonding is seen in stromeyerite, AgCuS (Frueh, 1955) and freieslebenite, $PbAgSbS_3$ (Hellner, 1957).

The Ag–S distances vary from 2·36 Å to 2·58 Å and the Sb–S distances vary from 2·48 Å to 2·58 Å. Scavnicar (1960) found that in the structure of stibnite (Sb_2S_3), the three shortest Sb–S bonds are 2·49, 2·57 and 2·58 Å, which is in good agreement with the present results. In the structure of stromeyerite, AgCuS (Frueh, 1955) and the structures of proustite, Ag_3AsS_3, and pyrargyrite, Ag_3SbS_3 (Harker, 1936), the Ag–S distance are 2·40 Å.

The temperature factors for the S atoms vary greatly by amounts considerably greater than the experimental error, which is itself large. Similar large discrepancies between the temperature factors of sulfur have been found in other sulfo-salts: in the structure of livingstonite, $HgSb_4S_8$ (Niizeki & Buerger, 1957*a*) the deviation of the temperature factor of sulfur (B_s) was 0·47 to 1·21; in jamesonite, $FePb_4Sb_6S_{14}$ (Niizeki & Buerger, 1957b), B_s varied 0·17 to 0·73; and in cosalite, $Pb_2Bi_2S_5$ (Weitz & Hellner, 1960), B_s varied from $-0{\cdot}009$ to 1·49. Transfer of valence electrons would have only a minor effect at low angles which would not explain this variation. Substitution of elements like Se and Te could cause a reduction of the temperature factor, but analyses given for livingstonite, jamesonite, cosalite and miargyrite have none present.

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Three-Dimensional Refinement of the Structure of Anthrone

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The crystal structure of anthrone has been refined on the basis of the disordered structure by two cycles of three-dimensional differential synthesis. The structure belongs to the space group $P2_1/a$ (C_{2h}^5). A molecule of anthrone is planar, and has no centre of symmetry, but on the basis of the disordered structure it possesses a centre of symmetry statistically.

Introduction

Anthrone crystallizes in the monoclinic system and belongs to the space group $P2_1/a$ (C_{2h}^5) (Srivastava, 1957). There are only two asymmetric molecules per unit cell. In the rotation photographs about the *b* axis, faint diffuse layer lines parallel to the regular layers were observed in positions corresponding to double the translation period of the *b* axis. The anomaly in the space group and the occurrence of diffuse layer lines were explained by assuming a disordered structure (Banerjee & Srivastava, 1960; Srivastava, 1961) in which the anthrone molecules were assumed to take two possible random orientations at 180° in the (010) plane while in the [010] direction there is no orientational disorder.

The crystal structure of anthrone has also been worked out and refined by successive cycles of two-dimensional difference synthesis (Srivastava, 1962). The value of

$$R = \frac{\Sigma||Fo|-|Fc||}{\Sigma|Fo|} \times 100$$

dropped to nearly 23% after the first cycle of difference synthesis from an initial value of 31%. A number of subsequent cycles of difference synthesis could not reduce R appreciably. To improve the agreement and derive coordinates to a higher degree of accuracy than had been obtained previously, the intensity data were completely revised and three-dimensional data for the reflexions $h0l$ to $h3l$ were collected, and the structure was refined by two cycles of three-dimensional differential synthesis.

Crystal data

Anthrone, $C_{14}H_{10}O$, molecular weight 194·22. Melting point, 154 °C. The molecule has no symmetry centre. Space group $P2_1/a$, with the following cell dimensions:

$$a=15{\cdot}80\pm0{\cdot}03,\ b=3{\cdot}998\pm0{\cdot}005,\ c=7{\cdot}86\pm0{\cdot}016\ \text{Å},$$
$$\beta=101°\ 40'\pm10',\ Z=2,\ D_m=1{\cdot}332\ \text{g.cm}^{-3}\ \text{and}$$
$$D_x=1{\cdot}335\ \text{g.cm}^{-3}.\ \mu=7{\cdot}88\ \text{cm}^{-1}\ \text{for Cu}\ K\alpha$$

radiation.

Experimental

A set of six to nine equi-inclination Weissenberg photographs, with each exposure time related to the next roughly by a factor of three, were prepared for each layer line from the zero to the third layer, with the crystal mounted along the *b* axis. The maximum possible value of the *k* index was five for Cu $K\alpha$ radiation, but on account of the limitation of the camera design, reflexions only up to the third layer could be recorded in the *b* axis setting. A Nonius integrating Weissenberg camera as described by Wiebenga & Smits (1950) was used. The crystal was mounted along the needle axis (the *b* axis) and therefore the linear dimensions of the spots parallel to the rotation axis remained constant for various spots during the rotation of the crystal. Extension of the