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The Crystal Structure of Barium Thiosulphate Monohydrate

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Crystals of $BaS_2O_3.H_2O$ are orthorhombic, space group $D_{2h}^{14}(Pbcn)$, with

$$a = 20{\cdot}07,\ b = 7{\cdot}19,\ c = 7{\cdot}37\ \text{Å}\ .$$

The structure has been determined by three-dimensional Fourier methods and refined by Booth's differential synthesis using hkl ($k = 0, 1, 2, 3, 4$) data ($R = 0{\cdot}13$).

The crystal structure is built up from slabs of two kinds, one formed by two layers of Ba^{2+} and $S_2O_3^{2-}$ the other by a layer of H_2O, succeeding one another along [100]. Each Ba^{2+} coordinates five $S_2O_3^{2-}$ and a H_2O molecule.

Hydrogen-bonding interactions are discussed.

Introduction

The structure analysis of $BaS_2O_3.H_2O$ was undertaken in this laboratory in 1956 (Cavalca, Nardelli & Braibanti) when the only reliable structure determination of compounds containing the $S_2O_3^{2-}$ group was that of $Na_2S_2O_3.5H_2O$ (Taylor & Beevers, 1952).

While the coordinates of Ba^{2+} were easily determined from $P(U, W)$ and $P(U, V)$ Patterson syntheses, overlapping and the presence of the heavy atom made difficult the complete determination by two-dimensional analysis. For these reasons this investigation has been taken up again, using three-dimensional methods.

In the meantime two other structures concerning thiosulphates have been published: $Na_2S_2O_3$ (Sándor & Csordás, 1961) and $Mg(OH_2)_6S_2O_3$ (Nardelli, Fava & Giraldi, 1962).

Experimental

Crystals of $BaS_2O_3.H_2O$, obtained by slow crystallization from aqueous solution, are orthorhombic colourless needles, elongated along the b axis with {100} faces predominating. The unit-cell dimensions and space group were determined from rotation and Weissenberg photographs around [010] and [001] (Cu $K\alpha$ radiation).

Crystal data

$BaS_2O_3.H_2O$, $M = 267{\cdot}5$, orthorhombic,
$a = 20{\cdot}07 \pm 0{\cdot}01$, $b = 7{\cdot}19 \pm 0{\cdot}01$, $c = 7{\cdot}37 \pm 0{\cdot}01$ Å.
$U = 1063{\cdot}5$ Å^3.
$Z = 8$, $D_x = 3{\cdot}337$, $D_m = 3{\cdot}447$ g.cm.$^{-3}$ (Clarke, 1877).
$\mu = 695$ cm.$^{-1}$ (Cu $K\alpha$).
$F(000) = 976$.
Space group $D_{2h}^{14}(Pbcn)$ (uniquely determined from systematic absences).

The intensities were evaluated by photometric measurements on multiple-film equi-inclination Weissenberg photographs (Cu $K\alpha$), using a thin needle (mean cross-section radius: 0·0025 cm.) for hkl ($k = 0, 1, 2, 3, 4$) and a fragment of nearly rectangular cross-section (0·02 cm. × 0·005 cm.) for $hk0$ reflections. These last reflections were used only to correlate the previous ones and to calculate the $P(U, V)$ Patterson projection, and were not introduced in the refinement since they were strongly influenced by absorption. The two equatorial Weissenberg photographs only were taken with the integrating camera of Wiebenga & Smits (1950).

78 independent $h0l$ reflections, 88 $h1l$, 124 $h2l$, 104 $h3l$ and 81 $h4l$ were observed, representing 81%, 47%, 66%, 63%, 51% respectively of the possible number observable (the layers with k odd are weaker).

The absorption correction for cylindrical samples was applied to the reflections obtained by rotation around [010]. For non-equatorial layers the correction for the shape of the spots was determined following the method of Phillips (1956). The structure amplitudes were derived by the usual formulae for Lorentz and polarization factors. The scaling factor was obtained at first by Wilson's method, then by comparison with the calculated values.

Determination of the structure

The development of the structural analysis can be outlined in the following steps:

(i) $P(U, W)$ and $P(U, V)$ Patterson syntheses were used to obtain a set of rough coordinates for Ba (Fig. 1; the Ba–S and Ba–O interactions reported in that figure have been deduced *a posteriori*).

(ii) $\varrho(X, Z)$ and $\varrho(X, Y)$ Fourier syntheses, calculated using the signs of Ba contributions to F_c, could not be interpreted owing to overlapping involving the Ba atom. Nor were the difference maps,

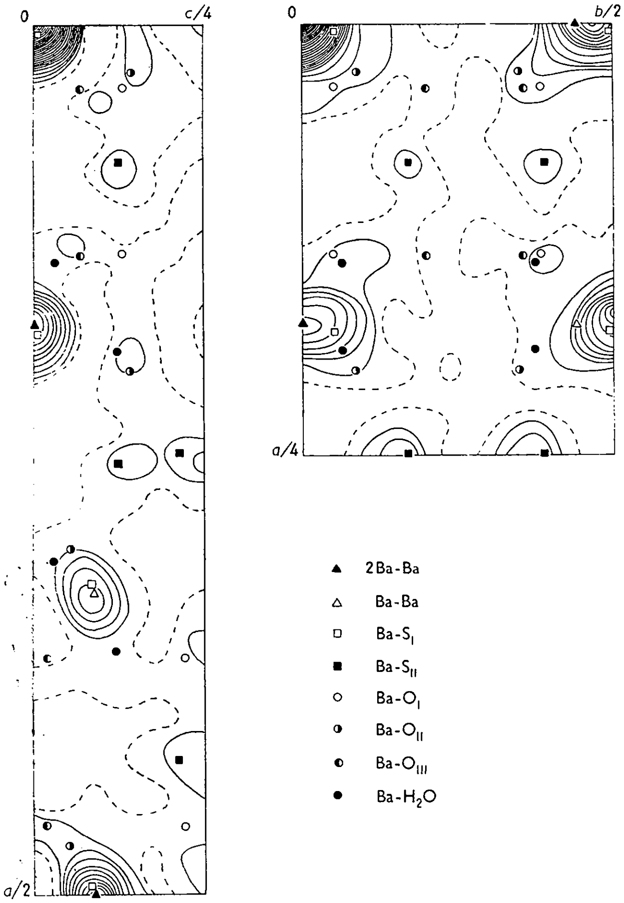

Fig. 1. $P(U, W)$ and $P(U, V)$ Patterson projections. Contours at arbitrary intervals.

calculated by subtracting the contributions of the heavy atom, useful.

(iii) To improve the coordinates of Ba, the three-dimensional distribution of the electron density in the region occupied by that atom was evaluated using the signs of the contributions of Ba alone to F_c's.

(iv) At this stage, the coordinates of Ba were sufficiently correct to allow its subtraction from the $\varrho(X, Z)$ map. This was now well resolved enough to show the peaks of two sulphur and three oxygen atoms.

(v) A complete view of the structure was achieved only from the generalized cosine and sine (010) projections C_1, C_2, C_3, C_4 and S_1, S_2, S_3, S_4 (the subscripts $1, \ldots, 4$ refer to the $h1l, \ldots, h4l$ reflections used in calculating these projections), calculated at first with the signs of Ba contributions alone to obtain the y coordinates of the other atoms, then with all the contributions.

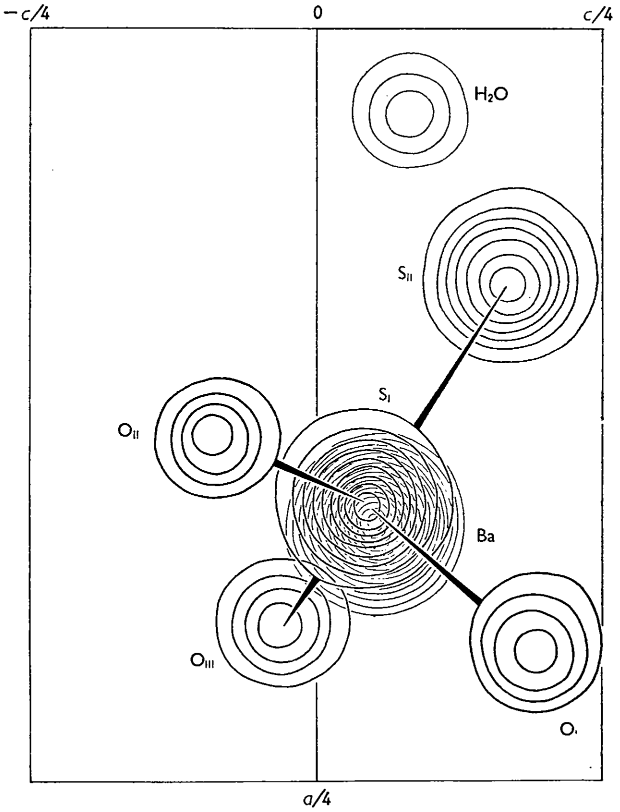

Fig. 2. Composite electron density map projected on (010). Contour intervals are 2·5 e.Å^{-3} for oxygen, 5 e.Å^{-3} for sulphur and 10 e.Å^{-3} for barium. Lowest contour is at 5 e.Å^{-3} in the case of O and S, at 10 e.Å^{-3} in the case of Ba.

Table 2. *Thermal parameters* (Å^2)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
Ba	0·93	0·31	0·59	−0·05	0·10	0·05
S$_I$	1·21	1·43	0·39	0·03	−0·04	−0·30
S$_{II}$	1·13	2·46	1·64	0·31	−0·11	−0·04
O$_I$	2·10	4·92	0·13	−1·53	0·18	−0·12
O$_{II}$	1·68	2·20	0·89	0·59	−0·18	0·12
O$_{III}$	0·33	0·71	1·75	−0·09	0·06	−0·12
H$_2$O	1·40	1·07	1·74	−0·18	−0·58	0·39

Table 1. *Final atomic coordinates and their standard deviations*

				x	y (Å)	z	$\sigma(x)$	$\sigma(y)$ (Å × 10^4)	$\sigma(z)$
	x/a	y/b	z/c						
Ba	0·1642	0·2194	0·0452	3·295	1·577	0·333	13	30	12
S$_I$	0·1582	0·7272	0·0412	3·175	5·229	0·304	42	64	39
S$_{II}$	0·0836	0·6092	0·1687	1·678	4·380	1·243	67	147	64
O$_I$	0·2017	0·8398	0·1798	4·048	6·038	1·325	343	592	287
O$_{II}$	0·1347	0·8691	−0·0973	2·703	6·249	−0·717	185	424	176
O$_{III}$	0·2021	0·5843	−0·0247	4·056	4·201	−0·182	200	387	216
H$_2$O	0·0256	0·1562	0·0758	0·514	1·123	0·559	214	541	317

Table 3. *Atomic peak heights* (e.Å^{-3}) *and curvatures* (e.Å^{-5})

		ϱ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{hk}	A_{kl}	A_{hl}
Ba	obs.	164·68	2053·9	783·9	2201·7	1·7	9·9	29·8
	calc.	168·40	2078·3	798·2	2225·1	3·8	4·4	19·9
S_{I}	obs.	51·37	656·6	371·7	681·5	−2·9	−8·8	4·4
	calc.	51·83	650·0	369·7	678·6	−3·2	−7·2	0·5
S_{II}	obs.	34·98	410·3	160·6	413·3	−25·4	1·4	9·1
	calc.	33·28	389·8	155·9	399·2	−26·6	2·5	10·8
O_{I}	obs.	12·50	80·6	40·0	92·5	−10·1	22·9	24·5
	calc.	10·76	70·9	35·6	71·8	−2·8	21·2	6·7
O_{II}	obs.	14·12	149·5	55·8	150·6	12·5	−12·8	27·7
	calc.	13·41	143·5	53·1	144·2	7·2	−13·3	27·4
O_{III}	obs.	13·55	138·5	61·2	123·0	−26·2	29·6	9·1
	calc.	14·19	145·8	61·3	134·6	−27·8	31·0	8·0
H_2O	obs.	11·22	129·2	43·7	83·7	−34·6	10·8	2·8
	calc.	11·72	131·9	46·1	88·5	−31·0	10·9	0·4

(vi) Refinement was carried out first by a three-dimensional ϱ synthesis (Fig. 2), then by a three-dimensional (F_o-F_c) synthesis and finally by five cycles of Booth's differential synthesis, two with isotropic and three with anisotropic thermal parameters.

The calculations were performed on an IBM 650 computer using the programmes of Brown, Lingafelter, Stewart & Jensen (1959) for structure factors and Fourier syntheses, and those of Shiono (1957, 1959) for differential synthesis and refinement of thermal parameters. In all these calculations the f curves

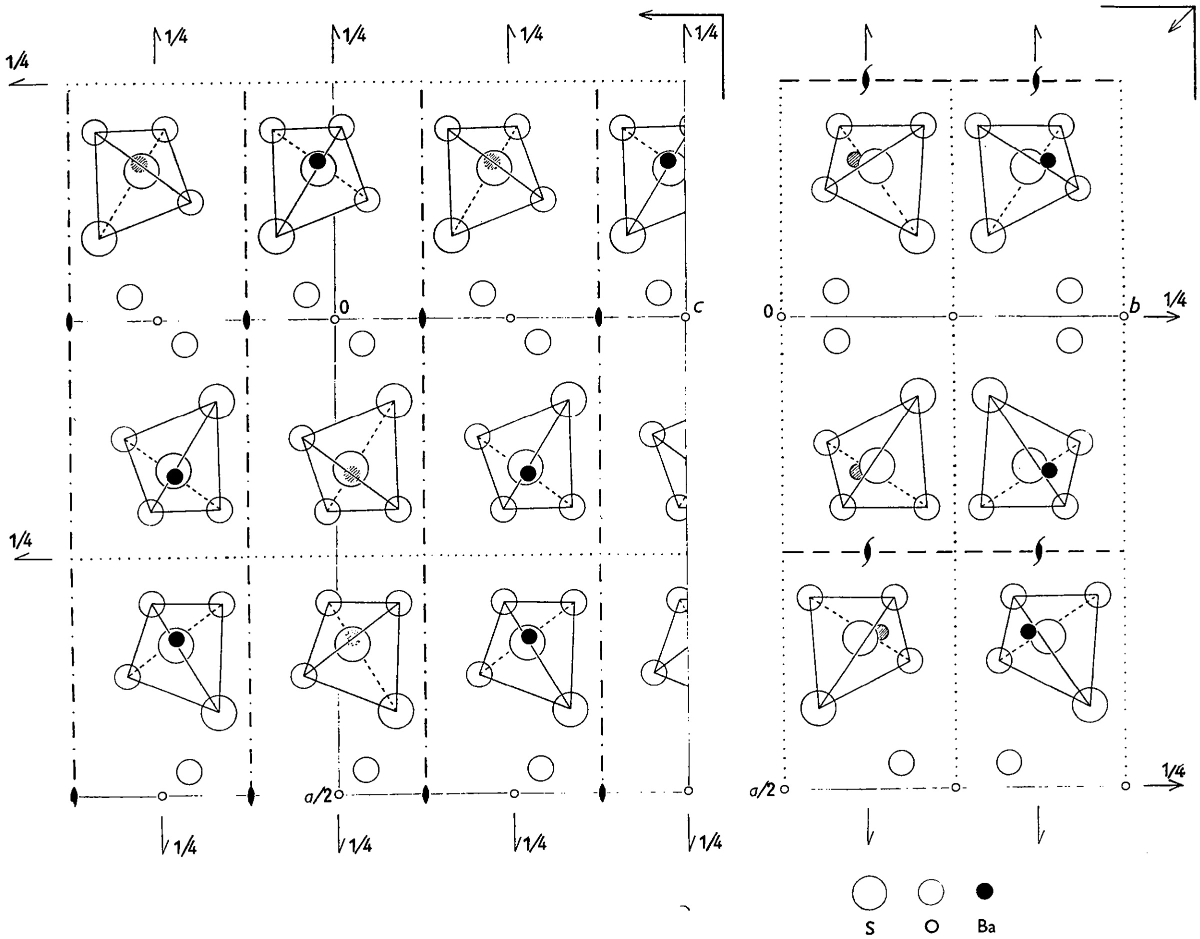

Fig. 3. Diagrammatic projections of the structure on (010) and (001).

were those of Thomas & Umeda (1957) for Ba^{2+}, of Dawson (1960) for S and of Berghuis *et al.* (1955) for O.

The final coordinates with their standard deviations (Cruickshank, 1949) are reported in Table 1. The standard deviation of the electron density is $\sigma(\varrho)=1{\cdot}09$ e.Å^{-3}.

Thermal parameters reported in Table 2 are influenced by the omission of reflections with $k \geq 5$, as shown by the peak heights and their derivatives

Table 4. *Observed and calculated structure factors*

A minus sign for F_o means 'less than'

h k l	10 $\lvert F_o \rvert$	10 F_c
2 0 0	2543	-2393
4	3198	-3239
6	3927	4463
8	2333	-2029
10	1953	-1782
12	3115	3221
14	475-	-134
16	2280	-2472
18	1361	1352
20	528-	-296
22	1488	-1718
24	1584	1928
0 0 2	2913	4314
1	2153	-2597
2	1783	-2023
3	939	-754
4	1931	-1930
5	1298	1164
6	3832	4330
7	2079	-1906
8	972	-866
9	475	376
10	2353	-2254
11	1953	1742
12	2133	2196
13	1900	-1783
14	770	-636
15	1056	-1025
16	1731	-1691
17	1277	1227
18	2016	1966
19	550	-545
20	506-	-60
21	485-	-239
22	1404	-1592
23	1003	1200
24	1066	1115
25	232-	-453
0 0 4	1329	1224
1	2111	-2066
2	1172	-1151
3	402-	32
4	665	-579
5	2733	2982
6	1741	1765
7	2575	-2750
8	717	-670
9	1615	-1506
10	907	-832
11	2375	2558
12	1077	1046
13	1847	-1969
14	538-	-334
15	538-	-338
16	802	-740
17	2121	2348
18	1066	1128
19	1414	-1482
20	432-	160
21	770	-901
22	770	-874
23	1235	1344
0 0 6	517-	126
1	2893	-2670
2	517-	-2
3	528-	-342
4	528-	74
5	2807	2724
6	1045	-817
7	2185	-2156
8	538-	-464
9	750	-652
10	675	697
11	2228	2426
12	517-	77
13	1668	-1615
14	485-	308
15	982	-757
16	432-	27
17	1731	1885
18	422	-422
19	1056	-1083
0 0 8	1921	-1851
1	1783	-1806
2	634	604
3	538	-455
4	770	800
5	1731	1714
5	1162	-1277
7	1077	-1131
8 0 8	686	616
9	402-	-209
10	528	686
11	1741	1739
12	1224	-1252
13	939	-1033
1 1 0	72-	86
3	738	-514
5	1044	810
7	1524	1433
9	768	-535
11	674	-493
13	297-	-143
15	415	-467
17	458	455
19	352-	282
21	327-	-329
23	275-	-102
25	187-	-160
1 1 1	327	-161
2	1579	-1658
3	887	542
4	1612	1891
5	815	-555
6	187-	-104
7	1565	-1274
8	2474	-2814
9	984	781
10	2023	1714
11	267-	200
12	285-	-45
13	302-	-113
14	2278	-2021
15	772	658
16	1994	1796
17	450	-471
18	352-	91
19	348-	-343
20	1439	-1567
21	322-	477
22	1150	1042
23	271-	-1
24	234-	267
25	178-	-33
1 1 2	688	641
2	213	309
3	183-	-13
4	1189	854
5	807	-529
6	1001	-656
7	577	496
8	768	-565
9	612	-539
10	271-	-161
11	285-	248
12	302-	-279
13	493	585
14	327-	87
15	569	-571
16	348-	375
17	352-	79
18	352-	118
19	343-	-125
20	331-	-465
21	314-	-286
22	285-	-95
23	255-	266
24	213-	168
1 1 3	1507	-1587
2	1705	-2039
3	1782	2042
4	1214	1098
5	1277	-1141
6	250-	-41
7	1261	-1140
8	1069	-918
9	1697	1593
10	1600	1400
11	539	-556
12	322-	43
13	776	-704
14	1298	-1337
15	1269	1311
16	509	594
17	352-	-336
18	343-	134
19	331-	-569
20	721	-681
21	1077	1149
22	883	855
23 1 3	221-	-319
24	162-	130
1 1 4	263-	61
2	781	-673
3	267-	67
4	271-	-154
5	280-	-287
6	289-	-193
7	297-	-50
8	306-	-67
9	314-	-283
10	501	583
11	335-	321
12	343-	-106
13	348-	364
14	612	-686
15	352-	-334
16	348-	3
17	339-	79
18	327-	66
19	306-	-1
20	285-	-99
21	250-	-124
22	213-	380
23	152-	151
1 1 5	1532	-1497
2	310-	-18
3	2210	2104
4	314-	235
5	1010	-998
6	446	494
7	560	-689
8	415	-442
9	1659	1752
10	348-	35
11	916	-1020
12	352-	263
13	874	-1001
14	348-	-50
15	1273	1513
16	327-	329
17	310-	-287
18	289-	-91
19	637	-687
20	230-	-154
21	1133	1305
1 1 6	484	-499
2	484	-481
3	343-	50
4	484	513
5	415	276
6	352-	-97
7	352-	132
8	352-	-282
9	352-	15
10	352-	183
11	348-	-180
12	339-	-24
13	331-	-232
14	318-	-144
15	302-	18
16	280-	101
17	255-	261
18	225-	89
19	187-	244
1 1 7	403	-426
2	612	734
3	1261	1298
4	556	-496
5	763	-820
6	343-	132
7	828	-894
8	424	583
9	1395	1398
10	624	-597
11	518	-498
12	289-	87
13	666	-600
14	696	693
15	1197	1264
16	446	-402
17	577	-648
1 1 8	310-	-33
2	306-	-167
3	581	228
4	302-	511
5	297-	-353
6	289-	9
7	280-	-143
8	267-	-290
9 1 8	255-	146
10	238-	-13
11	221-	-7
12	195-	51
13	162-	83
1 1 9	217	-270
2	763	843
3	649	717
4	930	-1008
5	187-	-382
6	174-	-119
7	148-	-140
2 2 0	1243	1955
4	1621	2318
6	2228	-4250
8	1418	1051
10	2354	2440
12	2894	-2855
14	1315	703
16	2228	1985
18	2193	-2164
20	347-	220
22	1701	1552
24	1188	-1304
0 2 1	1212	-1310
1	1453	-1639
2	1161	-700
3	666	-340
4	1170	855
5	869	604
6	469	184
7	1608	-1416
8	234-	-10
9	252-	241
10	270-	305
11	1360	924
12	1261	-864
13	1539	-1143
14	334-	-98
15	999	-651
16	562	459
17	752	795
18	361-	189
19	356-	-349
20	342-	358
21	320-	-259
22	292-	-92
23	725	859
24	445	-354
0 2 2	1895	-3434
1	1764	2018
2	1374	1210
3	194-	-74
4	2101	2042
5	2070	-1834
6	2638	-3095
7	2205	1730
8	1116	837
9	527	419
10	2341	2045
11	1647	-1339
12	2809	-2623
13	1436	983
14	707	549
15	356-	439
16	1778	1648
17	1256	-1241
18	1705	-1706
19	482	632
20	334-	285
21	562	542
22	1157	1186
23	851	-895
24	847	-1115
0 2 3	1594	-1668
1	1238	-1121
2	234-	195
3	1179	901
4	909	674
5	1472	1199
6	1486	-1258
7	1557	-1258
8	288-	-11
9	675	-429
10	1004	769
11	324-	81
12	582	-587
13	347-	3
14	356-	190
15	361-	190
16 2 3	361-	522
17	504	606
18	347-	-378
19	334-	-341
20	310-	227
21	707	-675
22	409	357
23	347	397
0 2 4	1557	-1369
1	2364	2648
2	829	565
3	419	375
4	1009	913
5	2408	-2561
6	1468	-1296
7	2214	2200
8	540	393
9	693	518
10	1053	928
11	2269	-2366
12	1216	-1245
13	1688	1671
14	365-	216
15	590	777
16	823	769
17	1584	-1801
18	703	-827
19	1013	983
20	275	135
21	617	622
22	571	550
0 2 5	1026	-875
1	455	-440
2	878	622
3	599	-375
4	334-	346
5	338-	343
6	1733	-1560
7	347-	178
8	351-	131
9	356-	127
10	752	858
11	361-	382
12	361-	-540
13	361-	-12
14	351-	396
15	342-	-225
16	329	474
17	306-	-18
18	792	-869
19	252-	42
20	217-	52
21	158-	129
0 2 6	562	421
1	2391	2428
2	361-	-15
3	361-	123
4	361-	-188
5	2314	-2392
6	361-	227
7	1967	2022
8	361-	-107
9	634	452
10	356-	-147
11	1909	-2075
12	342-	289
13	1387	1401
14	314-	-59
15	716	674
16	270-	-163
17	1661	-1756
18	207-	74
19	648	924
0 2 7	851	-801
1	356-	122
2	356-	48
3	356-	-77
4	712	627
5	351-	-237
6	347-	-408
7	338-	397
8	334-	363
9	324-	279
10	310-	496
11	302-	-172
12	1261	-1214
13	265-	267
14	238-	159
15	211-	-4
16	464	641
0 2 8	1486	1412
1	1725	1508
2	779	-665
3	302-	28
4	712	-685
5	1616	-1555
6	1360	1335
7	1153	1264
8	383	-428
9	356	302
10	720	-750
11	1134	-1333
12	716	976
0 2 9	199-	-298
1	522	590
2	324	282
3	347	382
4	175-	222
5	292	-454
1 3 0	958	-1214
3	1152	1708
5	1279	-1436
7	1128	-1175
9	1238	1194
11	354-	-111
13	393-	-270
15	850	937
17	433-	-311
19	488	-572
21	862	936
23	282-	-47
1 3 1	786	695
2	1564	2508
3	678	-546
4	1497	-1943
5	465	-168
6	354	101
7	377	-208
8	1306	1244
9	659	-609
10	1664	-1627
11	810	724
12	381-	-90
13	845	607
14	1322	1310
15	563	500
16	640	-763
17	429-	-51
18	424-	-261
19	409-	2
20	1037	991
21	357-	-342
22	946	-928
23	270-	290
24	198-	-257
1 3 2	758	-990
2	512	430
3	949	996
4	893	-887
5	374	-336
6	690	585
7	838	-783
8	901	862
9	1159	1094
10	393	-308
11	472	-451
12	417	228
13	870	-682
14	424	459
15	838	1003
16	493	-502
17	429-	-205
18	417-	-133
19	397-	-290
20	766	636
21	735	724
22	298-	-221
23	242-	-260
1 3 3	461	522
2	540	680
3	1033	-1285
4	1417	-1688
5	544	621
6	337-	225
7	719	703
8	1370	1246
9	1287	-1405
10	524	-483
11	758	666
12	417-	7

Table 4 (*cont.*)

h k l	$10\|F_o\|$	$10\ F_c$	h k l	$10\|F_o\|$	$10\ F_c$	h k l	$10\|F_o\|$	$10\ F_c$	h k l	$10\|F_o\|$	$10\ F_c$	h k l	$10\|F_o\|$	$10\ F_c$	h k l	$10\|F_o\|$	$10\ F_c$
13 3 3	853	728	12 3 5	424-	140	2 3 8	659	553	22 4 1	271	-288	18 4 3	938	837	17 4 5	306	-316
14	580	432	13	548	606	3	496	-542	0 4 2	1508	2308	19	280-	565	18	880	959
15	1152	-1262	14	405-	218	4	845	-715	1	991	-1103	20	245-	-156	0 4 6	459	-460
16	898	-905	15	1250	-1355	5	603	477	2	903	-945	21	202-	183	1	1543	-1605
17	612	558	16	365-	91	6	302-	-98	3	358	264	0 4 4	1274	1350	2	356-	110
18	397-	-218	17	901	770	7	286-	256	4	1596	-1281	1	1876	-2238	3	352-	-60
19	731	647	18	302-	-89	8	591	583	5	1888	1770	2	341	-263	4	352-	222
20	1136	1025	19	858	822	9	429	-451	6	1883	1759	3	414	-441	5	1600	1672
21	965	-912	20	194-	33	10	436	-372	7	1339	-993	4	976	-796	6	349-	140
22	254-	-312	1 3 6	429-	396	2 4 0	1056	-1505	8	1106	-840	5	1856	1882	7	1442	-1419
1 3 4	354-	-192	2	1068	1003	4	1271	-1312	9	934	-738	6	884	812	8	345	409
2	961	1021	3	433-	0	6	1971	2858	10	1390	-1183	7	1240	-1277	9	329-	-307
3	457	448	4	853	-928	8	739	-618	11	1199	1060	8	348-	-213	10	318-	-174
4	365-	-427	5	429-	-183	10	1933	-1953	12	2162	2008	9	352-	92	11	1741	1570
5	374-	-112	6	429-	4	12	2212	1977	13	387	-327	10	624	-635	12	742	-466
6	381-	22	7	429-	161	14	926	-664	14	356-	-264	11	1618	1798	13	1117	-1044
7	393-	-84	8	829	873	16	1413	-1229	15	356-	2	12	995	882	14	248-	-68
8	898	998	9	417-	-125	18	2273	2111	16	1305	-1214	13	1095	-1046	15	573	-472
9	616	516	10	603	-676	20	299-	5	17	1019	952	14	345-	-55	16	180-	194
10	965	-922	11	401-	88	22	1355	-1192	18	1153	1158	15	746	-732	0 4 7	1362	1359
11	500	-388	12	386-	-43	0 4 1	378	491	19	758	-597	16	573	-607	1	544	-555
12	429-	58	13	370-	188	1	1286	1707	20	275-	-133	17	1297	1154	2	792	-738
13	433-	-388	14	833	711	2	165-	-236	21	593	-490	18	486	384	3	313-	-72
14	949	1215	15	321-	-205	3	359	311	22	773	-809	19	559	-492	4	696	-772
15	505	469	16	508	-538	4	433	-280	0 4 3	1527	2047	20	188-	-158	5	452	423
16	481	-633	17	246-	-80	5	1650	-2052	1	1286	1388	0 4 5	1914	2307	6	1608	1515
17	389-	-124	1 3 7	1087	859	6	938	861	2	631	-725	1	348-	81	7	590	-495
18	361-	-59	2	465	-429	7	1646	1809	3	371	333	2	926	-877	8	505	-437
19	330-	-248	3	1326	-1129	8	271-	-17	4	773	-800	3	352-	30	9	264-	-70
20	481	579	4	747	604	9	1041	833	5	1244	-1219	4	945	-996	10	1033	-901
21	242-	294	5	401-	212	10	631	-532	6	1642	1675	5	489	-450	11	551	393
1 3 5	556	453	6	393-	96	11	2040	-1920	7	1125	1011	6	1557	1758	12	1045	1126
2	405-	324	7	700	507	12	424	385	8	525	-551	7	356-	140	13	375	-381
3	1358	-1494	8	814	-641	13	1608	1509	9	332-	143	8	826	-749	0 4 8	797	-797
4	412-	-24	9	1155	-1111	14	352-	-280	10	800	-844	9	356-	245	1	968	-907
5	961	901	10	484	395	15	359	441	11	1171	-1310	10	797	-907	2	616	525
6	421-	262	11	700	611	16	356-	-294	12	1049	1157	11	345-	-434	3	230-	140
7	1056	1173	12	306-	81	17	1535	-1550	13	965	923	12	1321	1465	4	559	557
8	429-	-151	13	817	773	18	452	473	14	356-	-304	13	325-	208	5	1106	1061
9	1291	-1515	14	242-	-401	19	1194	987	15	513	484	14	310-	-248	6	1052	-1027
10	433-	-336	15	810	-972	20	294-	-53	16	815	-888	15	291-	-52	7	872	-1056
11	429-	367	1 3 8	333-	303	21	486	409	17	835	-904	16	1156	-1062			

which are listed in Table 3. This omission is responsible for difference observed for the peak heights of the two sulphur atoms, which can be accounted for by residual effects of Ba on S_I, these atoms being nearly one above the other along [010].

The F_c structure factors reported in Table 4 are calculated with the coordinates and thermal parameters of Tables 1 and 2. The corresponding R (observed reflections only) and R' values (including $F_o=\frac{1}{2}F_{\text{min.}}$ when $F_c \geq F_{\text{min.}}$ for unobserved reflections) are

k	$R(hkl)$	$R'(hkl)$
0	0·087	0·090
1	0·127	0·170
2	0·161	0·184
3	0·141	0·155
4	0·119	0·126
Overall	0·128	0·144

The R value for the equatorial layer is considerably better than the others because the $h0l$ intensities have been measured on integrated photographs.

Discussion

The projections on (010) and (001) shown diagrammatically in Fig. 3 give a general view of the structure. The distances and angles in the pyramidal (C_{3v}) thiosulphate group agree fairly well with those found in the other thiosulphates of known structure (Table 5).

The standard deviations are calculated from the formulae of Ahmed & Cruickshank (1953) for bond lengths and of Darlow (1960) for angles, taking into account the effect of symmetry where necessary.

Each barium atom coordinates nine oxygen and two sulphur atoms at the following distances. (When the coordinates are not indicated the atom is at x, y, z)

Table 5. *Distances and angles in* $S_2O_3^{2-}$ *group*

	$BaS_2O_3.H_2O$	$Na_2S_2O_3.5H_2O$	$Na_2S_2O_3$	$Mg(OH_2)_6S_2O_3$
S_I–S_{II}	1·961 ± 0·010 Å	1·97 Å	2·01 ± 0·02 Å	2·020 ± 0·008 Å
S_I–O_I	1·568 ± 0·041	1·59	1·52 ± 0·03	1·484 ± 0·014
S_I–O_{II}	1·519 ± 0·032	1·46	1·46 ± 0·03	1·479 ± 0·040
S_I–O_{III}	1·439 ± 0·032	1·40	1·42 ± 0·03	
O_I–S_I–O_{II}	105·3 ± 2·3°	104–115°	109·4 ± 3·6°	110·9 ± 1·1°
O_I–S_I–O_{III}	104·3 ± 1·9		107·9 ± 3·6	111·0 ± 1·1
O_{II}–S_I–O_{III}	116·3 ± 1·4		114·4 ± 3·6	
S_{II}–S_I–O_I	109·7 ± 1·3		108·3 ± 2·4	107·6 ± 0·8
S_{II}–S_I–O_{II}	112·0 ± 0·8		109·3 ± 2·4	108·5 ± 0·8
S_{II}–S_I–O_{III}	108·7 ± 1·3		107·6 ± 2·4	

Ba–S_{II}	$3·362 \pm 0·013$ Å
Ba–O_{III}	$2·780 \pm 0·037$
Ba–O_{I} $(x, y-1, z)$	$3·000 \pm 0·055$
Ba–O_{II} $(x, y-1, z)$	$2·792 \pm 0·039$
Ba–S_{II} $(x, 1-y, z-\frac{1}{2})$	$3·440 \pm 0·008$
Ba–O_{I} $(x, 1-y, z-\frac{1}{2})$	$2·829 \pm 0·030$
Ba–O_{II} $(x, 1-y, \frac{1}{2}+z)$	$2·775 \pm 0·020$
Ba–$O_{III}$$(x, 1-y, \frac{1}{2}+z)$	$3·553 \pm 0·025$
Ba–O_{I} $(\frac{1}{2}-x, y-\frac{1}{2}, z)$	$2·997 \pm 0·036$
Ba–$O_{III}$$(\frac{1}{2}-x, y-\frac{1}{2}, z)$	$2·900 \pm 0·023$
Ba–H_2O	$2·827 \pm 0·023$

The two Ba–S distances are nearly of the same magnitude and remarkably longer than the corresponding distance in BaS of 3·19 Å (Goldschmidt, 1927); they lie in the range (3·18$_0$–3·52$_8$ Å) of Ba–S distances found in barium tetrasulphide monohydrate (Abrahams, 1954). The values of Ba–O distances are in agreement with those found in the coordination of oxygen by barium, as shown in Table 6.

Table 6. Ba–O *distances*

Compound	Distances (Å)	Source
BaO	2·772	Goldschmidt, 1927
$BaFeSi_4O_{10}$ (Gillespite)	2·73; 2·98	Pabst, 1943
$Ba_3(PO_4)_2$	2·71 –3·23	Zachariasen, 1948
$Ba(HCOO)_2$	2·67 –3·70	Sugawara, Kakudo, Saito & Nitta, 1951
$BaAl_2Si_2O_8$ (High temperature modification of Barium Felspar)	3·05	Yoshiki & Matsumoto, 1951
BaO_2	2·68; 2·79	Abrahams & Kalnajs, 1954
$BaS_4.H_2O$	2·787; 2·796	Abrahams, 1954
$BaTiO_3$	2·78 –2·96	Vousden, 1956
$BaBOF_3$	2·86	Chackraburtty, 1957
Celsian (Barium Felspar)	2·667–3·421	Newnham & Megaw, 1960
$BaZnO_2$	2·64 –3·36	v. Schnering, Hoppe & Zemann, 1960
$Ba(ClO_4)_2.3H_2O$	2·82 –3·00	Mani & Ramaseshan, 1960
$BaS_2O_3.H_2O$	2·78 –3·55	Present study

The environment of Ba^{2+} is illustrated by the stereographic and clinographic projections shown in Fig. 4 and 5 respectively. This environment corresponds to an octahedral arrangement of five $S_2O_3^{2-}$ groups and one H_2O molecule around each Ba^{2+}, three O–O and two O–S edges of $S_2O_3^{2-}$'s being directed towards Ba^{2+}. Conversely five of the six edges of each $S_2O_3^{2-}$ are orientated towards five Ba^{2+}, the sixth edge (O_{II}–S_{II}) towards a H_2O molecule.

The coordination polyhedra are linked together in such a way that the structure as a whole can be described as constituted from slabs of two kinds: one formed by two layers of Ba^{2+} and $S_2O_3^{2-}$, the other by a layer of H_2O. These slabs succeed one another along the [100] axis. Within each slab the Ba^{2+} and $S_2O_3^{2-}$ ions have an arrangement of NaCl type.

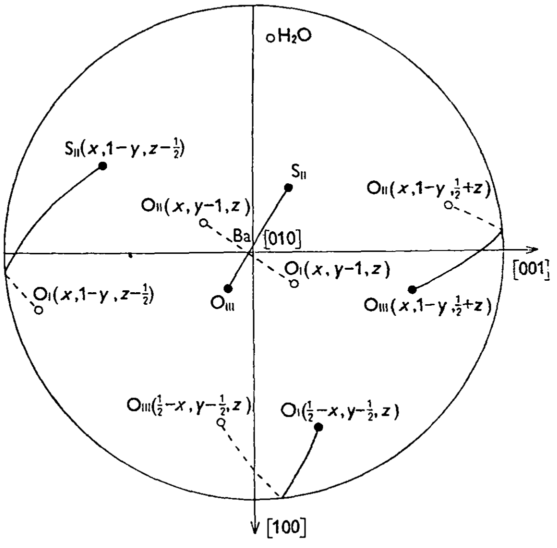

Fig. 4. Stereographic projection of the environment of Ba^{2+}.

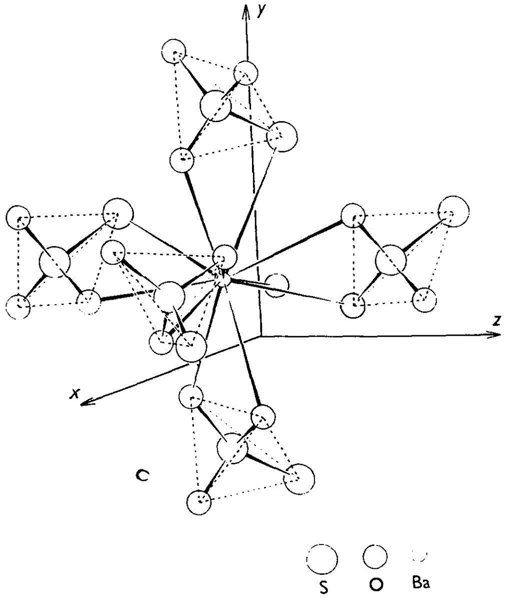

Fig. 5. Clinographic projection of the environment of Ba^{2+}.

The presence of the heavy atoms does not allow the direct location of H atoms. Nevertheless it is possible to get some information about their distribution by considering the bond interactions involving water molecules. Assuming for these a tetrahedral configuration with a lone pair pointing towards Ba^{2+}, the most probable orientation of the H's and of the other lone pair should be that represented in Fig. 6 on the basis of Donohue's (1952) angular criterion.

Each water molecule can form hydrogen bonds with two others related one by a symmetry centre and one by a 2-fold axis (Fig. 3) so that there would be two H atoms, generated by these symmetry elements,

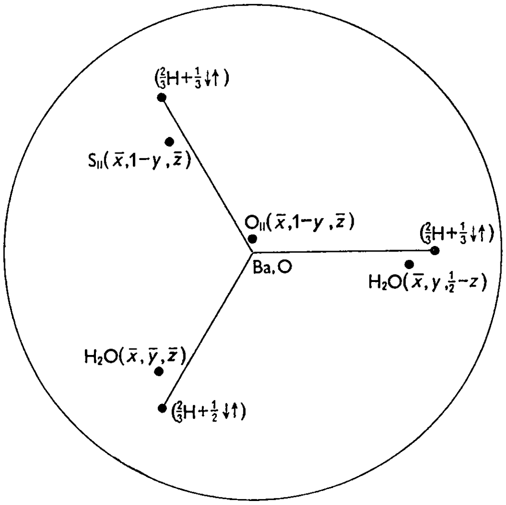

Fig. 6. Stereographic projection of the environment of a H_2O molecule viewed down the Ba–OH_2 bond.

between each H_2O couple. Steric hindrance between these two H atoms, especially in the case of 2-fold axis, indicates that a statistical distribution of H's among the three directions favoured for hydrogen bonding is probable. This kind of disordering is similar, in some aspects, to that observed in ice (Pauling, 1935; Peterson & Levy, 1957; Honjo & Shimaoka, 1957) and involves the possibility of hydrogen bonding with sulphur.

Fig. 7 shows a layer of H_2O molecules and their tetrahedral coordination. The tetrahedra are linked together in chains running along [001]. The hydrogen bonding distances are:

H_2O–H_2O $(\bar{x}, \bar{y}, \bar{z})$	2·713 ± 0·094 Å
H_2O–H_2O $(\bar{x}, y, \frac{1}{2}-z)$	2·766 ± 0·059
H_2O–S_{II} $(\bar{x}, 1-y, \bar{z})$	3·300 ± 0·037

The packing distances shorter than 4 Å are:

O_I–O_{II} $(x, 2-y, \frac{1}{2}+z)$	2·983 ± 0·057 Å
O_I–O_{III} $(\frac{1}{2}-x, \frac{1}{2}+y, z)$	3·015 ± 0·052
O_I–O_{III} $(\frac{1}{2}-x, \frac{3}{2}-y, \frac{1}{2}+z)$	2·961 ± 0·039
O_I–O_{III} $(x, 1-y, \frac{1}{2}+z)$	3·748 ± 0·061
O_{II}–H_2O $(x, 1+y, z)$	3·268 ± 0·050
O_{II}–H_2O $(x, 1-y, z-\frac{1}{2})$	3·260 ± 0·033
H_2O–$O_{II'}$ $(\bar{x}, 1-y, \bar{z})$	3·227 ± 0·029
H_2O–S_{II}	3·528 ± 0·053
H_2O–S_{II} $(x, 1-y, z-\frac{1}{2})$	3·633 ± 0·038
S_{II}–O_{III} $(x, 1-y, \frac{1}{2}+z)$	3·562 ± 0·025
S_{II}–S_{II} $(\bar{x}, y, \frac{1}{2}-z)$	3·563 ± 0·013

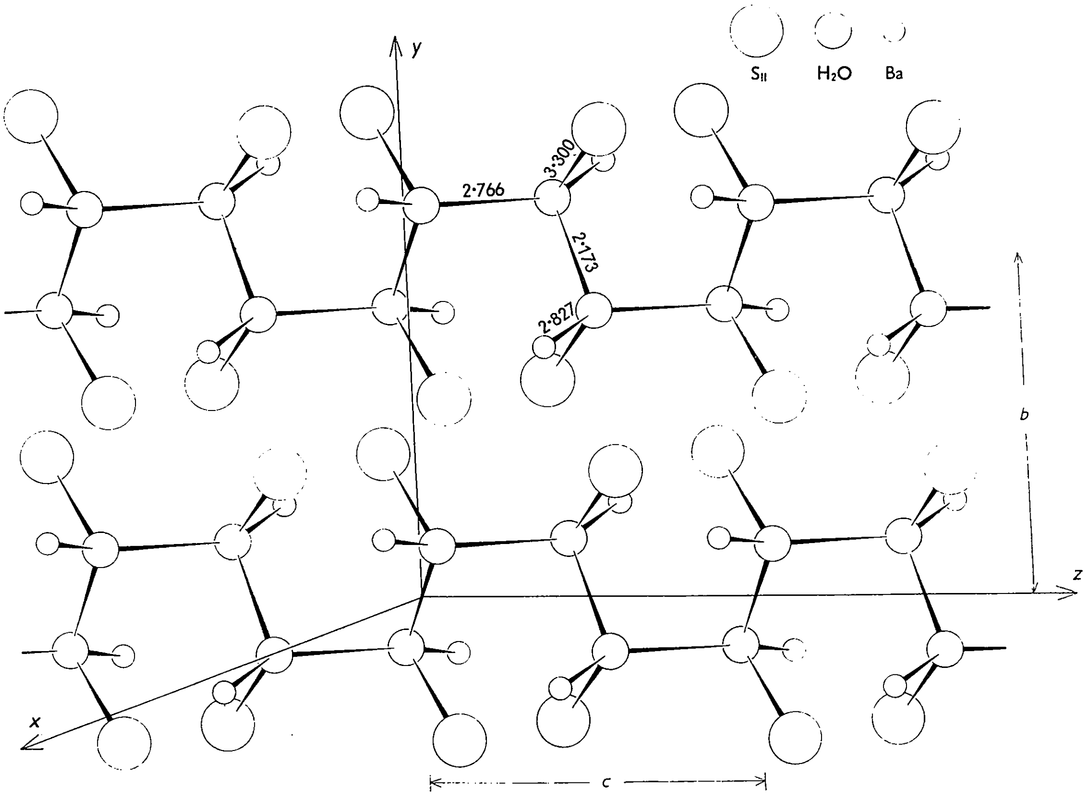

Fig. 7. A layer of H_2O molecules, showing two chains of water coordination tetrahedra.

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References

ABRAHAMS, S. C. (1954). *Acta Cryst.* **7**, 423.

ABRAHAMS, S. C. & KALNAJS, J. (1954). *Acta Cryst.* **7**, 838.

AHMED, F. R. & CRUICKSHANK, D. W. J. (1953). *Acta Cryst.* **6**, 385.

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

BROWN, B. W., LINGAFELTER, F. C., STEWART, J. M. & JENSEN, L. H. (1959). *Acta Cryst.* **12**, 350.

CAVALCA, L., NARDELLI, M. & BRAIBANTI, A. (1956). *Ric. Sci.* **26**, 1881.

CHACKRABURTTY, D. M. (1957). *Acta Cryst.* **10**, 199.

CLARKE, F. W. (1877). *Amer. J. Sci.* [3], **14**, 283.

CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.

DARLOW, S. F. (1960). *Acta Cryst.* **13**, 683.

DAWSON, B. (1960). *Acta Cryst.* **13**, 403.

DONOHUE, J. (1952). *J. Phys. Chem.* **56**, 502.

GOLDSCHMIDT, V. M. (1927). *Geochemische Verteilungsgesetze der Elemente* VIII. Oslo: Dybwad.

HONJO, G. & SHIMAOKA, K. (1957). *Acta Cryst.* **10**, 710.

MANI, N. V. & RAMASESHAN, S. (1960). *Z. Kristallogr.* **114**, 200.

NARDELLI, M., FAVA, G. & GIRALDI, G. (1962). *Acta Cryst.* **15**, 227.

NEWNHAM, R. E. & MEGAW, H. D. (1960). *Acta Cryst.* **13**, 303.

PABST, A. (1943). *Amer. Min.* **28**, 372.

PAULING, L. (1935). *J. Amer. Chem. Soc.* **57**, 2680.

PETERSON, S. W. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 70.

PHILLIPS, D. C. (1956). *Acta Cryst.* **9**, 819.

SÁNDOR, E. & CSORDÁS, L. (1961). *Acta Cryst.* **14**, 237.

SCHNERING, H. G. VON, HOPPE, R. & ZEMANN, J. (1960). *Z. anorg. Chem.* **305**, 241.

SHIONO, R. (1957). *Technical Report* No. 2, University of Pittsburg, Computation and Data Processing Center.

SHIONO, R. (1959). *Technical Report* No. 9, University of Pittsburg, Computation and Data Processing Center.

SUGAWARA, T., KAKUDO, M., SAITO, Y. & NITTA, I. (1951). *X-Rays (Osaka University)*, **6**, 85.

TAYLOR, P. G. & BEEVERS, C. A. (1952). *Acta Cryst.* **5**, 341.

THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.

VOUSDEN, P. (1956). *Acta Cryst.* **9**, 141.

WIEBENGA, E. H. & SMITS, D. W. (1950). *Acta Cryst.* **3**, 265.

YOSHIKI, B. & MATSUMOTO, K. (1951). *J. Amer. Ceram. Soc.* **34**, 283.

ZACHARIASEN, W. H. (1948). *Acta Cryst.* **1**, 263.

Acta Cryst. (1962). **15**, 484

The Structure of Salamander Alkaloids. I. On the Structure of Samandarine-Hydrobromide

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Samandarine $C_{19}H_{31}O_2N$ and the related compounds are the only genuine alkaloids so far known in animals. X-ray analysis shows that the sterol skeleton of samandarine is related to 5β-androstane. The oxazolidine ring as deduced by chemical methods has been confirmed.

The X-ray analysis has been mainly carried out on the hydrobromide with space group $P2_1$,

$$a=12{\cdot}98,\ b=6{\cdot}28,\ c=12{\cdot}43\ \text{Å};\ \beta=95°.$$

There are 2 molecules and 2 methanols in the unit cell. The heavy atom was found from Patterson projections. The heavy-atom technique was used to derive signs, and several 2-dimensional syntheses were calculated until the R_1-factor for the $h0l$ reflections reached 0·28. A 3-dimensional model of the molecule has been found and two 3-dimensional Fourier-syntheses were calculated. The R_1-factor reached 0·25 including unobserved reflections. The least-squares refinement was calculated using the program of Levy & Busing for the IBM 704. For the 3-dimensional intensities the final R_1-factor reached $R_1=0{\cdot}17$ including unobserved reflections.

Introduction

The miliary glands of the salamander species 'Salamandra maculosa' and 'Salamandra atra Laur' contain a secretion which has been studied by C. Schöpf and his co-workers. The main part of this secretion consists of proteins and water and only a small fraction of about 10% is a mixture of various alkaloids. Samand-