Acta Cryst. (1962). **15**, 317

The Crystal Structure of S-Methylisothiourea Sulphate $[CH_3SC(NH_2)_2]_2^+ SO_4^{2-}$

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(*Received* 5 *June* 1961)

Crystals of S-methylisothiourea sulphate are orthorhombic with space group *Pcan*. The unit-cell dimensions are:

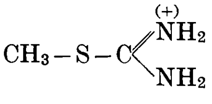
$$a = 8{\cdot}38,\ b = 11{\cdot}32,\ c = 12{\cdot}60 \text{ Å}\ .$$

The structure was refined by least squares using three-dimensional X-ray data obtained with Cu $K\alpha$ radiation. The final R-factor for 882 observed and 324 non-observed reflections was 15·2%.

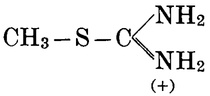
The $SC(NH_2)_2$ part of the molecule is planar. The two C–S bonds have lengths of 1·79 and 1·74 Å. The C–S–C angle is 104°. The SO_4 ion does not deviate significantly from a regular tetrahedron; the average S–O distance is 1·463 Å.

Introduction

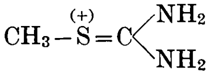
Simple valence-bond considerations predict resonance in the S-methylisothiourea ion between configurations I, II and III:



I



II



III

This would lead to one essentially single C–S bond and one of partial double-bond character. One would expect III to have the largest contribution since here the positive charge is on the less electronegative atom.

An accurate structure determination has been reported for thiourea by Kunchur & Truter (1958), and it is interesting to compare their results with those for S-methylthiourea sulphate. An additional point of interest is the SO_4-ion for which few accurate data are available.

Unit-cell data. Intensities

The crystals are orthorhombic. The following unit-cell dimensions were obtained from Straumanis-type oscillation diagrams:

$$a = 8{\cdot}38 \pm 0{\cdot}01,\ b = 11{\cdot}32 \pm 0{\cdot}01,\ c = 12{\cdot}60 \pm 0{\cdot}01 \text{ Å}\ .$$

By flotation the density was found to be 1·54 g.cm.$^{-3}$, agreeing with the calculated value for $Z = 4$.

Systematic absences lead to the space group *Pcan*(*Pbcn*).

The crystals at our disposal were for the greater part needles in the [001] direction with the form {110} well developed and small faces of the forms {010}, {111}, {121} and {012}. A few crystals had a more isometric habit. Measurements on several crystals with the optical two-circle goniometer yielded $a:b:c = 0{\cdot}740:1:1{\cdot}117$, as compared with $0{\cdot}740:1:1{\cdot}113$ from the above X-ray data. The crystals showed good cleavage along (110). Weissenberg diagrams of the layers zero through four about the a-axis and zero through seven about the b-axis were taken with Cu $K\alpha$ radiation using the multiple-film technique. The intensities were measured visually by comparison with an intensity scale. Absorption corrections were not applied although absorption was not negligible, the cross sections of the crystals having dimensions of about 0·15 and 0·20 mm. for the a- and b-axis respectively, and μ being 52·2 cm.$^{-1}$.

The total number of independent reflections measured was 882. The number that could have been recorded on our films is 1206, the number within the reflection sphere being 1350 (systematic extinctions excluded). The 324 reflections that escaped observation were included in the least-squares refinement with values corresponding to one half the minimum observable intensities.

Structure determination

The structure was solved by means of Patterson and electron-density projections. There is

$$\tfrac{1}{2}\{[CH_3SC(NH_2)_2]_2^+ SO_4^{2-}\}$$

in the asymmetric unit and thus the sulphur atom of sulphate ion has to be at a special fourfold position. There are three fourfold positions in the space group *Pcan*, of which only 4c: $x, 0, \frac{1}{4}$; $\bar{x}, 0, \frac{3}{4}$; $\frac{1}{2}+x, \frac{1}{2}, \frac{1}{4}$; $\frac{1}{2}-x, \frac{1}{2}, \frac{3}{4}$; need be considered; the other two, being at centres of symmetry, are ruled out by the tetrahedral configuration of the sulphate ion. In the $0kl$ projection the position of the sulphate sulphur atom is thus fixed; those of the other sulphur and the oxygen atoms in the asymmetric unit could be approximately

Table 1. *Observed and calculated structure factors*

Between brackets the values corresponding to one half the minimum observable intensities are given for non observed reflexions

h k l	F_{obs}	F_{calc}
0 0 2	251	317
4	554	770
6	671	654
8	(28)	29
10	428	-388
12	(33)	63
14	405	-304
16	61	70
2 0 0	321	-371
1	165	228
2	623	-888
3	643	-891
4	212	262
5	326	-317
6	335	-308
7	620	-569
8	378	347
9	242	-258
10	256	220
11	562	-518
12	79	70
13	61	41
14	61	-59
15	200	-171
4 0 0	126	99
1	158	-202
2	331	-372
3	205	-195
4	442	-469
5	559	608
6	88	-86
7	335	-292
8	256	-238
9	363	351
10	(33)	-32
11	196	-164
12	(28)	-28
13	112	103
14	121	114
15	61	-74
6 0 0	270	-262
1	(28)	-64
2	(28)	-39
3	(33)	23
4	219	-173
5	340	316
6	186	194
7	65	32
8	289	-276
9	186	180
10	163	157
11	(28)	-34
12	107	-104
13	121	106
8 0 0	(33)	21
1	93	-74
2	289	286
3	(33)	55
4	(33)	5
5	98	-81
6	172	131
7	93	86
8	121	-94
9	56	42
10	(19)	29
10 0 0	75	-78
1	149	-160
2	61	65
3	70	69
4	56	58
5	75	-56
0 1 2	(9)	31
4	373	-366
6	391	-397
8	154	-145
10	522	-439
12	382	-309
14	(23)	-45
16	70	-67
1 1 0	517	-1043
1	289	-325
2	824	964
3	517	600
4	522	-564
5	354	328
6	47	46
7	219	228
8	79	52
9	(23)	13
10	149	126
11	158	121
12	242	-195
13	182	-142
14	210	173
15	70	69
16	98	-109
2 1 1	860	-1131
2	770	-954
3	401	-436
4	276	220
5	458	-469
6	102	-79
7	186	-192
8	206	-179
9	(23)	-14
10	(23)	37
11	(23)	29
12	(23)	29
13	130	104
14	(19)	12
15	79	62
3 1 0	284	238
1	405	-498
2	242	208
3	102	-104
4	224	-206
5	447	-482
6	238	243
7	205	186
8	(23)	-24
9	517	-422
10	51	-48
11	228	179
12	(23)	3
13	130	-122
14	(19)	-25
15	107	106
4 1 1	149	-143
2	345	350
3	(19)	50
4	461	441
5	70	-59
6	340	311
7	154	-131
8	484	410
9	196	-141
10	238	202
11	(23)	-25
12	(23)	46
13	(19)	-4
14	116	90
5 1 0	238	-283
1	107	123
2	182	-147
3	186	182
4	70	71
5	210	-175
6	382	-327
7	503	441
8	219	186
9	233	-204
10	116	-101
11	79	80
12	102	96
13	65	-62
14	(14)	0
6 1 1	265	243
2	135	-116
3	349	340
4	70	-54
5	205	173
6	61	-58
7	149	130
8	(23)	-42
9	(23)	6
10	51	38
11	42	-38
12	79	78
13	(14)	-25
7 1 0	210	162
1	65	-68
2	116	-63
3	84	-73
4	275	238
5	70	67
6	163	-130
7	(23)	-6
8	158	142
9	(23)	-26
10	116	-131
11	70	73
12	56	61
8 1 1	(23)	-15
2	(23)	36
3	126	118
4	79	-67
5	(23)	16
6	168	-131
7	(23)	12
8	79	-74
9	42	45
10	75	-74
9 1 0	84	84
1	140	142
2	102	-110
3	102	-94
4	65	51
5	61	32
6	56	-34
7	37	-34
8	(14)	-5
10 1 1	75	-67
2	(19)	-9
3	65	-75
4	(14)	9
5	23	-33
0 2 0	102	37
2	820	-1495
4	154	153
6	508	-453
8	65	-39
10	121	-123
12	275	228
14	210	-171
16	158	176
1 2 1	750	-743
2	303	-226
3	359	-406
4	247	-276
5	116	174
6	270	270
7	(23)	-30
8	196	-169
9	79	65
10	140	-123
11	233	176
12	(33)	11
13	(28)	-38
14	(23)	-38
15	(23)	-13
2 2 0	335	345
1	573	679
2	598	-656
3	51	-39
4	65	-21
5	448	446
6	219	-229
7	223	211
8	98	84
9	503	469
10	191	-174
11	(28)	7
12	130	109
13	317	280
14	(19)	-33
15	37	-41
3 2 1	233	246
2	298	316
3	84	-80
4	438	-380
5	149	143
6	359	307
7	186	-163
8	154	122
9	228	-191
10	102	-77
11	(28)	-13
12	121	104
13	(23)	18
14	(19)	17
15	(14)	18
4 2 0	354	388
1	61	56
2	689	655
3	168	-143
4	531	503
5	494	483
6	196	191
7	349	-297
8	(28)	23
9	359	313
10	107	93
11	98	-83
12	186	-149
13	144	128
14	88	-72
5 2 1	284	-261
2	(23)	6
3	102	109
4	(23)	38
5	144	129
6	75	65
7	126	-102
8	(28)	-56
9	102	89
10	(28)	14
11	65	55
12	(23)	6
13	42	-41
14	33	-30
6 2 0	56	88
1	(28)	2
2	116	100
3	275	-261
4	256	-218
5	214	-217
6	363	336
7	387	-351
8	130	-134
9	107	-108
10	144	140
11	233	-215
12	(19)	-12
13	(14)	-27
7 2 1	144	160
2	(28)	35
3	88	-105
4	(28)	-38
5	144	150
6	(28)	-41
7	(28)	-42
8	(28)	13
9	107	-101
10	56	49
11	42	35
8 2 0	359	-378
1	(28)	-38
2	(28)	-13
3	130	117
4	219	-188
5	(28)	19
6	(28)	-18
7	88	96
8	79	-80
9	(19)	-7
10	102	115
9 2 1	(23)	-27
2	65	57
3	(23)	-6
4	(23)	-12
5	(23)	47
6	(19)	-22
7	(19)	-12
8	(14)	-14
10 2 0	(19)	15
1	75	-98
2	(19)	35
3	79	88
4	(14)	-34
5	33	-34
0 3 2	84	158
4	713	821
6	629	619
8	638	587
10	247	228
12	210	180
14	182	148
1 3 0	680	-1029
1	605	-605
2	149	194
3	168	166
4	293	-315
5	182	170
6	177	189
7	79	96
8	331	-312
9	(23)	33
10	265	218
11	354	311
12	130	-115
13	(23)	-12
14	172	156
15	56	62
2 3 1	509	569
2	502	-531
3	942	1129
4	126	153
5	224	203
6	391	-369
7	172	160
8	(23)	-42
9	144	113
10	(28)	32
11	154	-130
12	112	-84
13	75	-61
14	102	79
15	70	-75
3 3 0	233	231
1	33	15
2	289	252
3	554	593
4	102	112
5	396	-398
6	135	153
7	349	303
8	210	-177
9	149	-126
10	(28)	4
11	126	108
12	65	-47
13	182	-171
14	(19)	-21
15	102	115
4 3 1	84	-82
2	419	-387
3	84	-68
4	116	121
5	(23)	38
6	284	-281
7	126	108
8	293	-264
9	(28)	-32
10	144	-130
11	126	105
12	172	-160
13	130	101
14	84	-66
5 3 0	93	80
1	247	-229
2	210	-178
3	112	113
4	154	129
5	279	-251
6	93	-82
7	93	67
8	214	191
9	140	-137
10	56	-52
11	224	181
12	93	88
13	61	-55
14	(14)	-42
6 3 1	340	-311
2	121	129
3	(23)	-6
4	102	-96
5	210	-206
6	(28)	-45
7	51	-47
8	88	76
9	(28)	-9
10	(23)	-47
11	(23)	-13
12	(19)	-22
13	(14)	51
7 3 0	321	247
1	56	48
2	102	-66
3	88	81
4	196	171
5	(28)	-32
6	158	-163
7	(28)	-31
8	121	117
9	(23)	5
10	107	-109
11	37	-49
8 3 1	88	-94
2	(28)	6
3	47	54
4	130	142
5	116	-133
6	79	72
7	(23)	-30
8	56	47
9	(19)	-24
10	79	97
9 3 0	42	32
1	61	37
2	130	-157
3	88	-102
4	(23)	-26
5	65	55
6	(19)	-28
7	65	-83
8	56	70
10 3 1	56	68
2	(19)	21
3	47	58
4	(14)	-14
5	(14)	35
0 4 0	587	742
2	461	418
4	848	1057
6	47	35
8	508	432
10	331	-262
12	182	154
14	270	-242
1 4 1	433	430
2	163	150
3	624	-636
4	116	-70
5	224	190
6	200	165
7	135	119
8	(28)	-12
9	242	-200
10	102	91
11	93	57
12	98	69
13	84	52
14	51	-19
2 4 0	179	-103
1	302	324
2	93	-49
3	558	-562
4	342	306
5	236	-252
6	316	-323
7	587	-600
8	135	120
9	130	-123
10	172	-152
11	326	-304
12	210	179
13	(28)	-10
14	(23)	-26
15	135	-149
3 4 1	210	161
2	382	379
3	335	315
4	377	-339
5	265	217
6	191	170
7	(28)	-22
8	79	40
9	135	112
10	149	-120
11	(33)	16
12	88	59
13	135	-109
14	(19)	-24
4 4 0	577	-663
1	466	491
2	354	-323
3	112	-105
4	345	-331
5	312	269
6	61	-83
7	191	-141
8	(33)	-15
9	238	207
10	(33)	39
11	135	-116
12	51	34
13	61	68
14	51	58
5 4 1	(28)	14
2	107	-105
3	135	-149
4	191	-156
5	(28)	-39
6	177	-145
7	(33)	-13
8	163	-159
9	(33)	13
10	75	-61
11	(28)	-10
12	65	-50
13	(19)	56
6 4 0	186	-133
1	224	205
2	242	212
3	(28)	-23
4	247	-212
5	144	114
6	(33)	40
7	(33)	41
8	200	-191
9	186	165
10	(23)	24
11	102	81
12	130	-134
7 4 1	79	-68
2	(33)	14
3	163	-172
4	112	120
5	56	60
6	112	113
7	61	-57
8	(23)	37
9	(23)	-8
10	(23)	41
11	56	66
8 4 0	(28)	14
1	(28)	17
2	219	188
3	84	72
4	56	-54
5	(28)	-30
6	168	166
7	65	75
8	(23)	-13
9	(19)	-31
9 4 1	61	72
2	(23)	31
3	(23)	-24
4	51	-71
5	(19)	29
6	(19)	-11
7	(14)	-15
10 4 0	33	40
1	56	-73
2	33	46
3	(9)	-3
0 5 2	70	58
4	461	-430
6	410	-409
8	79	-114
10	154	-142
12	(23)	-39
14	(23)	-30
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1	135	96
2	298	270
3	154	170
4	42	-52
5	512	-440
6	517	454
7	116	115
8	391	-350
9	112	-81
10	289	259
11	(28)	-35
12	172	-157
13	61	-71
14	47	78
15	42	55
2 5 1	419	-463
2	(19)	12
3	121	-162
4	238	238
5	484	-450
6	191	-183
7	130	-132
8	112	-81
9	65	53
10	(33)	-7
11	79	-66
12	140	-131
13	47	43
14	56	-58
3 5 0	47	-65
1	489	-559
2	135	-110
3	238	232
4	84	-64
5	284	-245
6	70	53
7	(28)	-33
8	121	-116
9	289	-277
10	126	100
11	112	111
12	(28)	-35
13	182	-177
14	51	52
4 5 1	75	-44
2	(28)	-27
3	293	-314
4	284	278
5	88	-74
6	205	167
7	70	53
8	238	219
9	(33)	-47
10	289	268
11	(33)	5
12	158	142
13	(23)	-5
5 5 0	(28)	45
1	196	-175
2	363	-355
3	307	316
4	(28)	17
5	182	-158
6	154	-148
7	130	129
8	(28)	15
9	(28)	33
10	(28)	-42
11	84	82
12	79	77
13	65	-82
6 5 1	396	369
2	93	91
3	284	302
4	(33)	-53
5	88	80
6	(33)	32
7	102	77
8	(28)	37
9	(28)	1
10	84	-73
11	93	-87
12	(14)	-8
7 5 0	270	268
1	65	-70
2	140	-121
3	65	67
4	116	126
5	61	79
6	98	-91
7	(28)	10
8	79	84
9	47	57
10	121	-122
8 5 1	88	-100
2	116	-141
3	(28)	6
4	84	-70
5	(28)	-43
6	79	-98
7	(23)	67
8	88	-111
9	70	93
9 5 0	(28)	56
1	56	44
2	(28)	-10
3	51	-52
4	56	79
5	(19)	19
6	37	-54
10 5 1	(14)	5
2	(14)	14
0 6 0	340	-344
2	419	-422
4	149	-126
6	782	-658
8	354	293
10	349	-324
12	200	181
14	(19)	-9
1 6 1	335	-290
2	79	-60
3	335	-297
4	88	-61
5	158	157
6	303	-271
7	177	-153
8	210	-170
9	(28)	-23
10	(28)	-21
11	121	90
12	79	-78
13	(28)	33
14	61	-51
2 6 0	158	-126
1	214	244
2	130	-134
3	70	-51
4	154	125
5	587	554
6	210	-198
7	79	57
8	303	238
9	400	333
10	158	-134
11	84	50
12	93	95
13	158	156
14	107	-109
3 6 1	(19)	-19
2	335	303
3	298	-263
4	93	54
5	107	-103
6	149	150
7	116	98
8	233	198
9	(33)	-11
10	56	52
12	(28)	50
13	(23)	-1
14	(19)	17
4 6 0	382	364
1	405	401
2	470	448
3	400	-350
4	126	115
5	98	80
6	210	164
7	112	-77
8	(33)	15
9	61	81
10	98	-72
11	130	-113
12	(28)	-36
13	140	154
5 6 1	56	47
2	130	-103
3	130	152
4	84	48
5	112	-101
6	(33)	-9
7	93	-58
8	(33)	-14
9	(28)	40
10	79	58
11	65	-60
12	(19)	34
6 6 0	349	-359
1	126	103
2	182	194
3	177	-186
4	93	-75
5	(33)	-15
6	98	93
7	130	-134
8	(33)	9
9	112	-110
10	163	157
11	102	-109
7 6 1	112	120
2	(33)	-1
3	65	-53
4	61	43
5	79	74
6	(28)	42
7	98	106
8	(23)	25
9	(19)	-1
10	(14)	-1
8 6 0	130	-133
1	(28)	-16
2	(28)	-1
3	(23)	14
4	154	-174
5	(23)	-35
6	56	54
7	51	54
8	88	-124
9 6 1	(23)	10
2	51	-48
3	(19)	49
4	47	-81
5	(14)	-4
0 7 2	536	535
4	107	102
6	442	379
8	461	384
10	191	164
12	154	136
14	51	50
1 7 0	88	-86
1	(14)	-34
2	121	-112
3	242	248
4	484	-481
5	107	95
6	298	233
7	349	300
8	345	-285
9	135	-70
10	219	191
11	(37)	65
12	140	-129
13	(19)	-19
14	70	103
2 7 1	419	438
2	158	-130
3	340	354
4	121	-114
5	247	213
6	84	-62
7	121	99
8	210	-167
9	(33)	45
10	(33)	-19
11	47	-60
12	(28)	33
13	88	-64
3 7 0	(19)	23
1	261	-309
2	177	150
3	275	231
4	70	46
5	205	-166
6	(33)	28
7	326	286
8	(33)	9
9	(33)	-5
10	88	72
11	186	193
12	126	-113
13	(19)	-17
4 7 1	(28)	-36
2	(28)	54
3	177	-162
4	177	-157
5	(33)	36
6	135	-109
7	(33)	11
8	116	-87
9	(33)	41
10	126	-102
11	88	76
12	75	-82
5 7 0	431	439
1	369	-361
2	(33)	-9
3	140	140
4	210	207
5	(33)	-7
6	(33)	37
7	(33)	2
8	(28)	36
9	154	-145
10	88	-71
11	(23)	31
6 7 1	102	-65
2	(33)	-5
3	126	-142
4	(33)	-13
5	(33)	-42
6	(33)	53
7	(28)	-42
8	(28)	-12
9	(23)	-19
10	(23)	-15
7 7 0	(33)	34
1	(33)	-19
2	154	-200
3	65	-64
4	116	115
5	102	-125
6	84	-77
7	(23)	-32
8	98	101
9	(19)	-31
8 7 1	(23)	-34
2	(23)	29
3	(23)	-32
4	(23)	37
5	(23)	-24
6	(19)	45
7	(19)	-47
9 7 0	(19)	-12
1	(19)	20
2	(14)	-44
3	(14)	-9
0 8 0	251	289
2	247	213
4	587	474
6	438	-325
8	414	349
10	144	-139
12	(28)	35
1 8 1	(28)	-19
2	65	-73
3	(28)	11
4	233	221
5	65	71
6	65	56
7	158	124
8	144	116
9	56	51
10	84	86
11	(23)	27
12	(23)	13
13	(19)	10
2 8 0	363	355
1	(23)	26
2	233	-186
3	345	-305
4	(23)	13
5	140	105
6	(28)	23
7	354	-341
8	200	181
9	(23)	-7
10	144	-130
11	168	-188
12	102	108
3 8 1	326	280
2	186	-121
3	410	354
4	(33)	18
5	88	85
6	107	-105
7	(33)	14
8	(23)	-31
9	(28)	-34
10	(23)	-18
11	(23)	-45
12	(19)	-32
4 8 0	331	-307
1	321	254
2	154	-138
3	303	-255
4	205	-182
5	154	140
6	121	-113
7	65	-53
8	88	-87
9	70	65
10	(23)	39
11	107	-133
0 9 2	130	-107
4	(28)	-15
6	126	104
8	224	-169
10	130	-123
12	(19)	-30
1 9 0	79	74
1	102	-62
2	373	371
3	102	-87
4	75	-73
5	368	-337
6	312	293
7	(28)	-22
8	140	-117
9	200	-205
10	112	115
11	(14)	-28
12	112	-114
2 9 1	233	-209
2	79	50
3	228	-199
4	284	-254
5	(28)	-37
6	(28)	-3
7	102	-93
8	(23)	9
9	(23)	-36
10	61	-57
11	56	38
12	37	25
3 9 0	302	-312
1	242	-201
2	(28)	-31
3	200	156
4	158	-123
5	210	-191
6	93	-89
7	98	96
8	(23)	19
9	205	-206
10	65	55
11	(19)	41
4 9 1	(33)	-25
2	102	81
3	(33)	-22
4	130	141
5	(33)	33
6	251	238
7	(28)	-78
8	84	79
9	(28)	-37
10	56	60
0 10 0	135	-122
2	624	-518
4	(28)	15
6	247	-210
8	172	162
10	84	-76
1 10 1	289	-243
2	130	-123
3	135	-117
4	70	-63
5	168	-134
6	140	-116
7	(28)	-26
8	84	-84
9	37	24
10	107	-99
11	(14)	15
2 10 0	345	271
1	126	105
2	(28)	-35
3	(28)	-32
4	242	213
5	303	275
6	121	-119
7	56	-56
8	51	-38
9	242	230
10	75	-85
11	(14)	7
3 10 1	186	-168
2	(28)	-52
3	(28)	-40
4	205	185
5	107	-96
6	65	75
7	70	-73
8	65	73
9	(23)	-39
10	88	89
4 10 0	121	113
1	224	183
2	(33)	30
3	163	-146
4	(28)	11
5	(28)	43
6	172	169
7	158	-153
8	(23)	15
9	65	78
10	(19)	45
0 11 2	(28)	12
4	(28)	59
6	(23)	60
8	88	85
10	121	100
1 11 0	424	-398
1	(28)	6
2	88	59
3	79	70
4	261	-220
5	163	-124
6	65	51
7	140	119
8	149	-137
9	(19)	0
10	79	69
2 11 1	210	171
2	(28)	12
3	(28)	52
4	(28)	-14
5	135	118
6	(23)	36
7	56	36
8	(23)	-33
9	(19)	-26
10	56	-50
3 11 0	70	-53
1	93	-78
2	172	157
3	275	253
4	(28)	30
5	(28)	17
6	(23)	8
7	238	233
8	(19)	1
9	(14)	-27
4 11 1	98	-77
2	(28)	9
3	(28)	11
4	121	-122
5	(28)	-21
6	75	-68
7	(23)	-9
8	(23)	-26
9	(19)	52
0 12 0	251	197
2	177	-136
4	238	222
6	102	-100
8	56	80
1 12 1	154	122
2	116	86
3	284	202
4	(23)	30
5	(23)	11
6	98	77
7	61	-34
8	121	80
2 12 0	158	166
1	112	92
2	126	-109
3	112	-106
4	121	111
5	75	61
6	(19)	-27
7	191	-142
8	(14)	31
3 12 1	102	116
2	70	-48
3	(23)	36
4	(23)	-9
5	70	87
6	70	-71
7	93	103
4 12 0	112	-102
1	75	98
2	70	-77
3	75	-90
4	65	-69
5	88	88
6	(23)	-19
0 13 2	84	-73
4	(14)	14
6	116	-107
1 13 0	(14)	-26
1	163	-102
2	307	256
3	(14)	3
4	(14)	-22
5	93	-77
6	154	130
2 13 1	42	-32
2	56	50
3	88	-88
4	42	33
5	37	-31
3 13 0	168	-160
1	75	-86
2	65	-64
3	37	53
4	84	-94
5	163	-187
0 14 0	149	114
2	191	-169
1 14 1	102	-75
2	51	22
3	107	-73
2 14 0	88	90
1	93	98
2	42	-49
3	37	-55
3 14 1	51	-80

found from the Patterson projection. Starting from these sulphur and oxygen coordinates it was possible to locate the other atoms by means of successive electron-density projections. A similar procedure was used for the *h0l* projection. These two projection were refined to *R*-factors of 21 and 22% respectively. The third projection along the *c*-axis was used to check the three-dimensional structure deduced from the *a*- and *b*-axis projections.

A three-dimensional least-squares refinement was then started. After three cycles with individual isotropic temperature factors the *R* factor had dropped from 26·7 to 19·6%. As it was clear from the projections that there was marked anisotropy in the electron distribution of the sulphur atoms, anisotropic temperature parameters were introduced for these atoms after the third cycle. After the fourth cycle *R* dropped to 16·1%. A number of low-order reflections showed rather poor agreement, caused partly by extinction. In order to examine the effect of this on the refinement, only reflections with sin $\theta > 0{\cdot}5$ were used in the next two cycles; *R* now dropped to 14·4%. When the low-order reflections after some minor improvements were included again, *R* for all reflections was 17·6%. Two more cycles were calculated, the final *R* being 15·2%. The final coordinates do not differ significantly from those of the refinement with the low orders omitted (largest difference 0·015 Å in the *y* of C_1; see Table 2). The final temperature factors, however, are consistently lower, but because of neglect of the absorption correction and omission of the hydrogen atoms the temperature parameters are not considered to be very reliable. A list of observed and calculated structure factors is given in Table 1. The scattering factors of Berghuis *et al.* (1955) for C, N and O, and those of Tomiie & Stam (1958) for S were used.

Results

In Table 2 the final coordinates are listed together with the calculated standard deviations. Bond distances are given in Fig. 1(*a*) and Table 3, bond angles in Fig. 1(*b*) and Table 4. Table 5 lists the temperature parameters. The principal vibration directions of the two sulphur atoms are given in Table 6. In Fig. 2 and 3 projections of the structure along the *a*- and *c*-axes are shown with the hydrogen bonds indicated by broken lines. The probable course of the (110) cleavage plane is indicated by the chain line in Fig. 3. In Fig. 2 the interionic distances shorter than 3·50 Å are indicated.

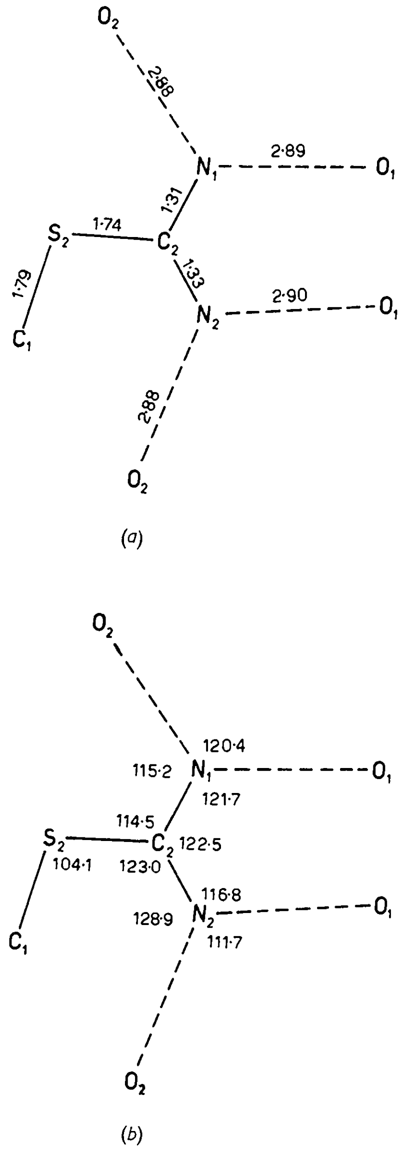

Fig. 1. Bond length and angles in the S-methylisothiourea ion.

Table 2. *Final coordinates and calculated standard deviations in* Å

Between brackets the coordinates resulting from the refinement with the low orders omitted

	x		σ(*x*)	*y*		σ(*y*)	*z*		σ(*z*)
S_1	3·5972	(3·5981)	0·0022	0·0000	(0·0000)	0·0000	3·1500	(3·1500)	0·0000
S_2	7·3531	(7·3500)	0·0023	2·6644	(2·6673)	0·0022	6·6251	(6·6268)	0·0020
O_1	4·4412	(4·4445)	0·0052	0·9698	(0·9679)	0·0055	2·4372	(2·4432)	0·0054
O_2	2·7519	(2·7526)	0·0050	0·6944	(0·6961)	0·0051	4·1108	(4·1108)	0·0050
N_1	6·2121	(6·2114)	0·0063	2·1957	(2·1957)	0·0066	4·3636	(4·3709)	0·0064
N_2	5·9691	(5·9686)	0·0059	0·4592	(0·4660)	0·0063	5·8750	(5·8691)	0·0057
C_1	7·9328	(7·9338)	0·0090	1·5174	(1·5319)	0·0088	7·8782	(7·8773)	0·0095
C_2	6·4084	(6·4061)	0·0066	1·6739	(1·6732)	0·0072	5·5467	(5·5445)	0·0064

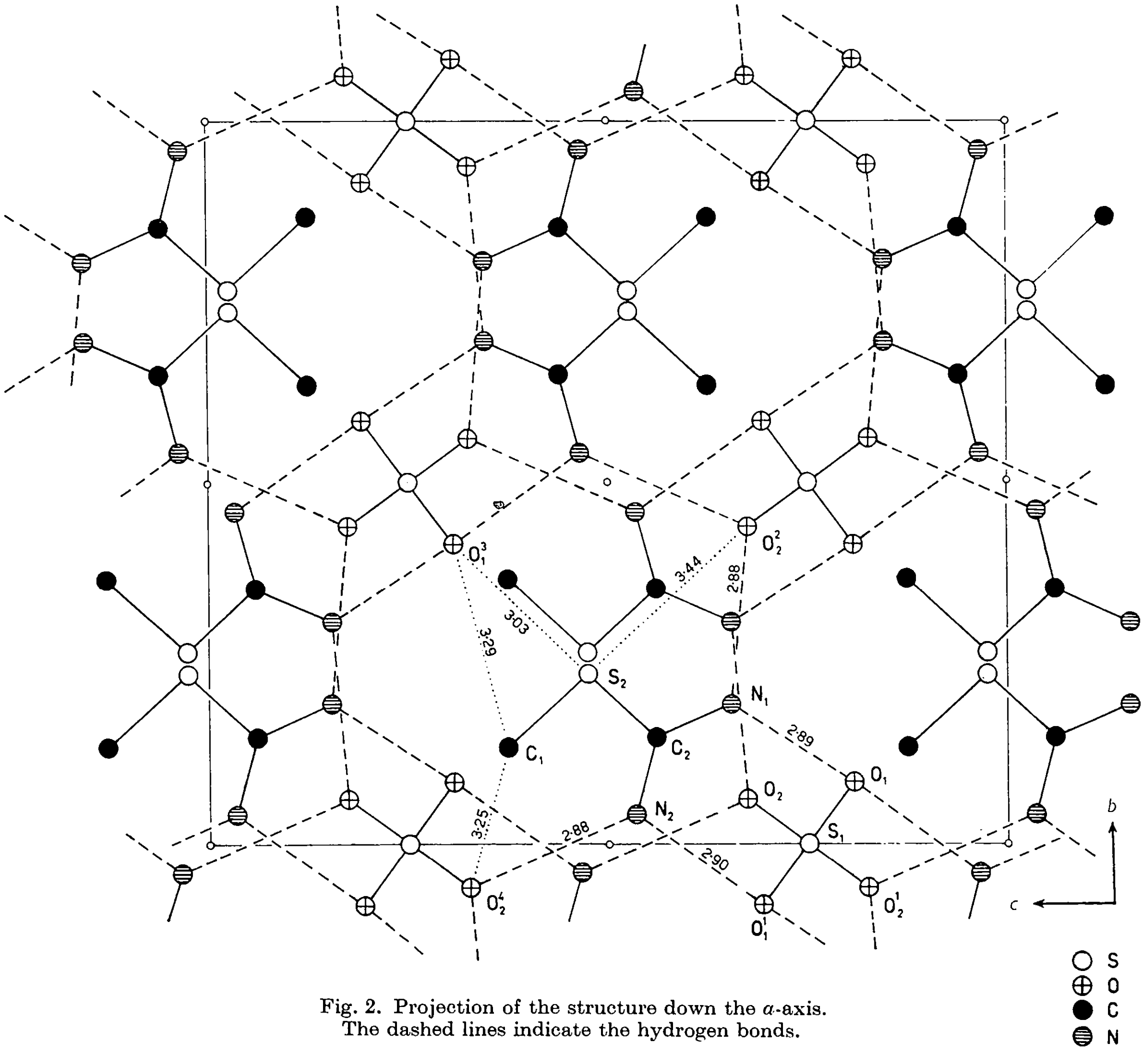

Fig. 2. Projection of the structure down the *a*-axis.
The dashed lines indicate the hydrogen bonds.

Table 3. *Bond distances and calculated standard deviations*

	Distance	σ
C_1–S_2	1·790 Å	0·009 Å
C_2–S_2	1·743	0·007
C_2–N_1	1·308	0·009
C_2–N_2	1·333	0·009
S_1–O_1	1·470	0·006
S_1–O_2	1·456	0·006
$N_1 \cdots O_1$	2·889	0·008
$N_1 \cdots O_2^2$	2·875	0·008
$N_2 \cdots O_1^1$	2·903	0·008
$N_2 \cdots O_2^4$	2·878	0·008

Table 4. *Bond angles and calculated standard deviations*

	Angle	σ
C_1–S_2–C_2	104·1°	0·4°
S_2–C_2–N_1	114·5	0·5
S_2–C_2–N_2	123·0	0·5
N_1–C_2–N_2	122·5	0·6
C_2–$N_1 \cdots O_1$	121·7	
C_2–$N_1 \cdots O_2^2$	115·2	
C_2–$N_2 \cdots O_1^1$	116·8	
C_2–$N_2 \cdots O_2^4$	128·9	
$O_1 \cdots N_1 \cdots O_2^2$	120·4	
$O_1^1 \cdots N_2 \cdots O_2^4$	111·7	
O_1–S_1–O_2	109·8	0·3
O_1–S_1–O_2^1	109·2	0·3
O_1–S_1–O_1^1	109·9	0·4
O_2–S_1–O_2^1	109·0	0·4

Discussion

The thiourea part of the molecule comprising S_2, C_2, N_1 and N_2 is practically planar. The best plane through these atoms, calculated with the method of Schomaker *et al.* (1959), is:

$$0·8435x - 0·4151y - 0·3409z = 2·8361 .$$

In view of the calculated standard deviations S_2 has been given three times the weight of the other atoms. The distances of S_2, C_2, N_1 and N_2 from this plane are 0·002, 0·016, 0·005 and 0·005 Å respectively. C_1 lies at 0·56 Å from this plane so that the C_1–S_2 bond makes an angle of 18° with it.

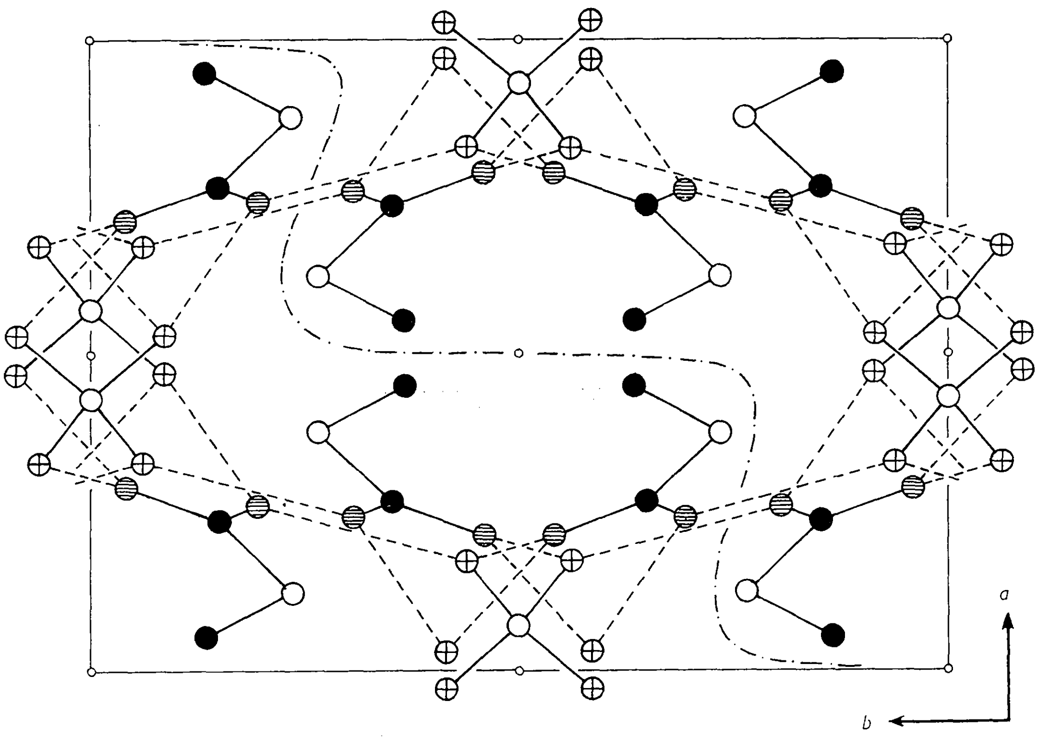

Fig. 3. Projection of the structure down the *c*-axis. The dashed lines indicate the hydrogen bonds. The chain line indicates the probable course of the (110) cleavage plane.

Table 5. *Temperature parameters* (Å^2)

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
S_1	0·0431	0·0260	0·0227	0·0000	−0·0019	0·0000
S_2	0·0710	0·0414	0·0541	0·0224	−0·0013	0·0402

	U
O_1	0·047
O_2	0·043
N_1	0·049
N_2	0·041
C_1	0·056
C_2	0·039

Table 6. *Direction cosines and mean square amplitudes of vibration for the axes of the vibration ellipsoids of* S_1 *and* S_2

	$\cos\alpha$	$\cos\beta$	$\cos\gamma$	$\overline{u^2}$
S_1	1	0	0	0·043
	0	0·966	−0·257	0·026
	0	0·257	0·966	0·022
S_2	0·832	−0·201	−0·517	0·086
	0·276	−0·659	0·700	0·047
	0·481	0·725	0·493	0·034

The C_1–S_2 bond length of 1·79 Å is that of a single bond, the single-bond distances for various compounds ranging from 1·78–1·84 Å (see Abrahams, 1956). The C_2–S_2 bond of 1·74 Å is 0·03 Å longer than the corresponding bond in thiourea (Kunchur & Truter, 1958), the difference being possibly significant. As little is known about the nature of the bonds involved detailed discussion of the results is hardly worth while. One may state that the C_2–S_2 bond has some double-bond character, probably a little less than in thiourea.

The C–S–C angle of 104° agrees very well with those in several other compounds in which sulphur is bound to two carbon atoms (see Sutton, 1958).

The C–N bonds do not differ significantly amongst themselves or from those in thiourea and are of intermediate double-bond character. There is, however, a large unexplained difference between the two S–C–N angles.

The four N–O-hydrogen bonds are medium strong and make angles of 6, 8½, 0 and 14° (in the order of Table 3) with the plane of the thiourea part of the molecule.

The SO_4 ion does not deviate significantly from a regular tetrahedron. The average S–O distance is 1·463(±0·004) Å. This distance is considerably shorter than the S–O distance of 1·488(±0·007) Å found by Atoji & Rundle (1958) in gypsum and that of 1·484 Å (no accuracy stated) found by Okaya *et al.* (1957) in monomethylammonium aluminium sulphate alum. The difference between our value and that of Atoji

& Rundle is three times the calculated standard deviation for the difference (0·008 Å) and thus would be significant. Other accurate data for the SO_4 ion are those of Singer & Cromer (1959) for zirconium sulphate; they found two significantly different S–O distances of 1·443 and 1·486 Å. It is possible that the calculated standard deviations are too low so that the above differences are not significant. It is also possible that one has to abandon the idea of the SO_4 ion being a regular tetrahedron of constant dimensions under all circumstances. More work on the SO_4 ion is needed to settle this question.

The author wishes to express his gratitude to Prof. E. G. Cox in whose laboratory most of the work was done and who suggested the subject, to Dr D. W. J. Cruickshank and Miss D. Pilling for their constant willingness to perform the necessary calculations on the Leeds University Ferranti Pegasus computer and to Prof. C. H. MacGillavry for advice. He is indebted to the Ramsay Memorial Fellowships Trust for the award of a fellowship.

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Search for an Anisotropic Debye-Waller Factor in Cubic Copper-Base Solid Solutions

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(*Received* 22 *June* 1961)

A re-examination has been made of the Debye–Waller temperature factor $\exp\{-2B(\sin\theta/\lambda)^2\}$, where B, according to Weiss and co-workers, is a varying function of $\{hkl\}$ when measurements are made on α brass powder. The integrated and peak intensities of several different lines from powder samples of α brass and α aluminium bronze were obtained at 77 °K. and room temperature, with Mo $K\alpha$ radiation, after heat treatments designed to induce varying amounts of short-range order. It was found that deviations of B from isotropy were marginal and not significant except possibly for the 222 lines. No deviations comparable in magnitude with those reported by Weiss and co-workers were found.

Weiss and co-workers (1956) reported measurements of integrated intensities of the 222 and 400 Mo $K\alpha$ lines diffracted by α brass powder at 77 and 295 °K., and showed that these intensities could not be reconciled with the conventional expression $\exp\{-2B(\sin\theta/\lambda)^2\}$ for the Debye–Waller attenuation factor associated with thermal vibrations (hereafter abbreviated DWF), unless B was taken to be a function of direction in the crystal, so that for a given temperature B was different for 222 and 400. They reached this conclusion both by comparing intensities of the same line at two temperatures, and also by comparing intensities of the two lines at one temperature (and comparing these ratios with computed ratios obtained for various assumed values of B). Values of B were expressed in terms of the Debye characteristic temperature Θ, which accordingly turns out to be effectively a function of crystal direction (we refer to this as an 'anisotropy of the Debye temperature'); values of Θ so obtained do not agree with those calculated from calorimetric measurements on α brass.

Weiss and co-workers believed that the anisotropy