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The Structure of Cycloalliin Hydrochloride Monohydrate

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The crystal structure of cycloalliin hydrochloride monohydrate, $C_6H_{11}NO_3S . HCl . H_2O$, has been solved by conventional methods. The space group is $P2_1$. The monoclinic cell has dimensions $a=5·292$, $b=12·375$, $c=8·447$ Å, $\beta=107·45°$. The sulfoxide oxygen is axial and the methyl group equatorial. Positional parameters and temperature factors are given for all atoms. The final value for R is 0·0390.

Introduction

There is considerable interest in the stereochemistry of sulfur since it can function as an asymmetric center; some isomeric forms have been shown to exhibit different biological activity. The first determination of the absolute configuration of a sulfur atom was made by Hine (1962) who determined the crystal structure of (+)-*S*-methyl-L-cysteine sulfoxide. He made use of the known configuration of a second asymmetric center in the molecule, the naturally occurring amino acid L-cysteine, to determine the absolute configuration of sulfur, a technique first suggested by Mathieson (1956).

The absolute configuration of (−)-menthyl-*p*-iodobenzenesulfinate has also been established (Fleischer Axelrod, Green & Mislow, 1964) by determining its crystal structure and utilizing the known configuration of the (−)-menthyl group. Recently the absolute configuration of a sulfoxide mustard oil was established by a determination of the crystal structure of a crystalline product formed with thiourea (Cheung, Kjaer & Sim, 1965).

To our knowledge the absolute configuration of a cyclic sulfoxide has not previously been determined. For this reason, and because cyclic sulfoxide L-5-methyl-1,4-thiazane-3-carboxylic acid 1-oxide (cycloalliin) is obtained from and is related to the aroma of onions (Virtanen & Matikkala, 1959), we decided to determine the crystal structure of cycloalliin hydrochloride monohydrate ($C_6H_{11}NO_3S . HCl . H_2O$). The structure of cycloalliin and the numbering system used in this investigation are shown in Fig. 1.

Experimental

The isolation and identification of cycloalliin was first reported by Virtanen & Matikkala (1959). Crystals of this material in the form of the hydrochloride monohydrate were grown from an acetone–water mixture acidified with hydrochloric acid. The crystals belong to the monoclinic sphenoidal class, and usually occur as trapezoidal plates or tablets. The optical and crystallographic properties have been described elsewhere (Jones, Lee, Black & Palmer, 1965).

Weissenberg photographs established the fact that the crystals are monoclinic with the probable space group $P2_1$ (C_2^2) since the only systematic absences were $0k0$ with k odd. The cell dimensions were obtained from 2θ scans with a single-crystal goniostat using copper radiation, $K\alpha_1=1·54051$ Å. The values obtained are:

$a=$ 5·292 ± 0·004 Å Unit-cell volume 527·87 Å^3
$b=$ 12·375 ± 0·008 $Z=2$
$c=$ 8·447 ± 0·006 $\varrho=1·456$ g.cm^{-3}
$\beta=$ 107·45 ± 0·02° $\varrho_{calc}=1·447$ g.cm^{-3}

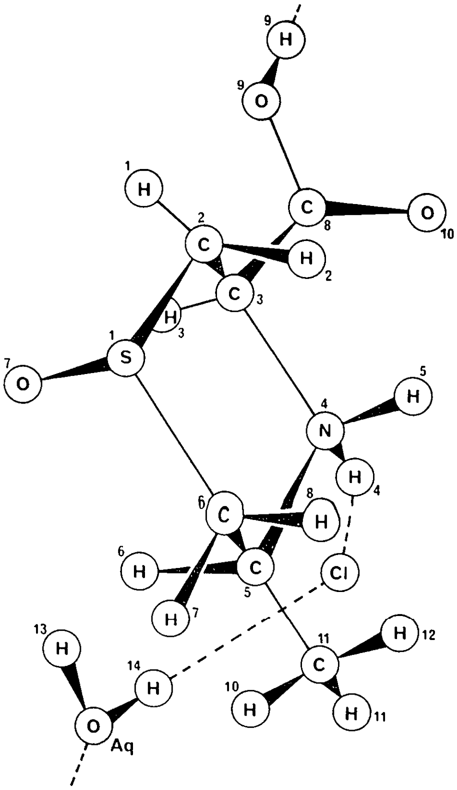

Fig. 1. Molecular configuration of cycloalliin. HCl . H_2O and the numbering system used in this investigation.

Intensities were obtained by means of a Picker scintillation counter and solid-state detector coupled with a General Electric XRD-5 diffractometer equipped with goniostat. The intensity data were collected by counting for ten seconds at the diffraction peak (4° take-off angle) with the crystal stationary. A total of 1219 intensities were measured, of which 38 were assigned a zero intensity. The crystals selected for the intensity determination had a maximum dimension of 0·05 mm. No correction was made for either absorption or extinction. The linear absorption coefficient for this crystal is 49·2 cm^{-1} for Cu $K\alpha$ radiation, and the maximum value of μR is 0·13.

Complete intensity data were obtained from two crystals because it was thought that the first crystal might have undergone radiation damage. The intensity data for the second crystal were obtained after installation of a magnetic shutter on the X-ray collimator which cut off the incident X-ray beam except when aligning the crystal and for the 10-second interval used to record an intensity. The second crystal thus received much less total irradiation than the first crystal. No obvious trends in the two sets of intensity data could be established, however; consequently for the final stages of least-squares refinement the two sets of intensities were summed in order to decrease the effect of random errors.

Calculations were made with an IBM 7044 computer using a full-matrix least-squares refinement program written by Gantzel, Sparks & Trueblood (1961) with modifications by A. Zalkin. The electron density and distance programs were written by A. Zalkin. The function minimized in the least-squares calculation was $\Sigma\, w(|F_o|-|F_c|)^2/\Sigma\, wF_o^2$, where w is the weighting factor and F_o and F_c are the observed and calculated structure factors. In this calculation, each independent reflection was assigned unit weight, including those for which $F(\text{obs})=0$.

Atomic scattering factors for Cl^-, neutral S, N, O, C, and H were taken from *International Tables for X-ray Crystallography* (1962). Dispersion corrections (Templeton, 1962) of $+0{\cdot}3$ electron were added to the S and Cl^- scattering factors. The imaginary part of the dispersion correction was neglected.

Refinement procedure

A three-dimensional Patterson function was calculated from all the data, and the positions of three atoms were readily deduced. The parameters for these three atoms, assumed to be chlorine, sulfur, and oxygen, were refined by least squares. The conventional discrepancy index R, defined as $\Sigma\, ||F_o|-|F_c||/|\Sigma\, |F_o|$, decreased from 0·71 to 0·35 after four cycles, and after three additional cycles, to 0·337.

The values obtained for the parameters of these three atoms were then used to calculate the phase angles for a three-dimensional electron-density map. With the aid of a model of the molecule it was possible to locate two additional oxygen and five carbon atoms. The parameters of these ten atoms were then refined by four cycles of least squares. This reduced R to 0·194. There remained three heavy atoms to be located; namely, one oxygen and one carbon of cycloalliin and the oxygen atom of water. Peaks due to the oxygen and carbon atoms of cycloalliin were found in the electron-density map with some certainty, but there appeared to be four possible positions for the water oxygen atom. Four cycles of least-squares refinement were calculated with the addition of the oxygen and carbon atoms of cycloalliin and oxygen atoms in two of the four possible positions for water. The temperature factor for one of the water oxygen atoms increased to 80; this was clearly not an acceptable position for the water molecule. The other three atoms had acceptable temperature factors.

Oxygen atoms were then assumed to occupy the other two possible positions for water suggested by the electron-density map, but after four cycles of least-squares refinement the temperature factor for these two oxygen atoms became very large. Consequently only one of the four peaks in the electron-density map actually represented the position occupied by the oxygen atom of the water molecule.

Further refinement was undertaken by giving sulfur, chlorine, four oxygen atoms and one carbon atom anisotropic temperature factors of the form $\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-2\beta_{12}hk-2\beta_{13}hl-2\beta_{23}kl)$. After four cycles of least-squares refinement R became 0·0577. At this stage all thirteen atoms were given anisotropic temperature factors and the parameters refined by two cycles of least squares. This reduced R to 0·0554.

A three-dimensional electron-density difference function with all atoms subtracted out except hydrogen was calculated from the results of the last anisotropic refinement. This allowed the positions of all fourteen hydrogens to be readily located. Four cycles of least-squares refinement were calculated with isotropic temperature factors for the hydrogen atoms and anisotropic temperature factors for the thirteen heavy atoms. This reduced R to 0·0461. As a final step the intensity data for the two crystals were summed and these data used for four additional cycles of least-squares refinement. This resulted in the final value for R of 0·0390.

The positional and thermal parameters and their calculated standard deviations for the final structure are listed in Tables 1 and 2 respectively. The observed and calculated structure factors are shown in Table 3.

Description of the structure

The molecular configuration of cycloalliin is shown in Fig. 1. The absolute configuration of the molecule was derived with the knowledge that the configuration about C(3) is L since this amino acid is from a natural source.

The six-membered ring has the chair conformation with interatomic distances and bond angles shown in

Tables 4 and 5 respectively. The ring conformation, bond angles, and distances are in good agreement with those found by Shearer (1959) for the α modification of 1,4-dithian 1,4-dioxide.

A point of particular interest is the configuration of the methyl group, sulfoxide oxygen, and carboxyl group with respect to the ring. The oxygen atom occupies the axial position, in agreement with that found for many other sulfoxides (Shearer, 1959; Johnson & McCants, 1964; Martin & Uebel, 1964; Cairns, Eglington & Gibson, 1964). The S–O bond distance of 1·492 Å is also in good agreement with the value found for those sulfoxides where sulfur is bonded to two carbons and one oxygen (Abrahams, 1956; Shearer, 1959). The two C–S–O angles are both slightly less than tetrahedral, as was found to be the case in both diethyl and dibenzyl sulfoxides (Abrahams, 1956) and in dithian disulfoxide (Shearer, 1959).

The methyl and carboxyl groups in the isomer used in this investigation are equatorial to the ring. The

Table 1. *Final positional parameters and standard deviations* (*in parentheses*)

	x	*y*	*z*
S	−0·0620 (2)	0·50 (0)	−0·0775 (1)
Cl	0·2261 (2)	0·0686 (1)	−0·2853 (1)
N	0·2684 (7)	0·3048 (3)	−0·1549 (4)
O(7)	−0·3150 (6)	0·4378 (3)	−0·1176 (5)
O(9)	0·3606 (7)	0·2307 (4)	0·2703 (4)
O(10)	0·6186 (7)	0·2108 (4)	0·1067 (4)
O(aq.)	−0·3630 (8)	0·1292 (5)	−0·4752 (5)
C(2)	0·1873 (8)	0·4197 (4)	0·0667 (5)
C(3)	0·2061 (8)	0·3057 (4)	0·0050 (5)
C(5)	0·0711 (9)	0·3615 (4)	−0·2953 (5)
C(6)	0·0566 (9)	0·4803 (4)	−0·2546 (5)
C(8)	0·4219 (9)	0·2437 (4)	0·1321 (6)
C(11)	0·1516 (9)	0·3462 (4)	−0·4513 (5)
H(1)	0·146 (15)	0·422 (10)	0·183 (12)
H(2)	0·346 (15)	0·460 (10)	0·095 (12)
H(3)	0·017 (15)	0·266 (10)	−0·028 (12)
H(4)	0·279 (15)	0·234 (10)	−0·193 (12)
H(5)	0·378 (15)	0·330 (10)	−0·142 (12)
H(6)	−0·097 (15)	0·320 (10)	−0·307 (12)
H(7)	−0·071 (15)	0·518 (10)	−0·352 (12)
H(8)	0·195 (15)	0·525 (10)	−0·242 (12)
H(9)	0·496 (15)	0·190 (10)	0·355 (12)
H(10)	0·041 (15)	0·383 (10)	−0·528 (12)
H(11)	0·143 (15)	0·256 (10)	−0·478 (12)
H(12)	0·304 (15)	0·399 (10)	−0·438 (12)
H(13)	−0·437 (15)	0·112 (10)	−0·412 (12)
H(14)	−0·279 (15)	0·116 (10)	−0·472 (12)

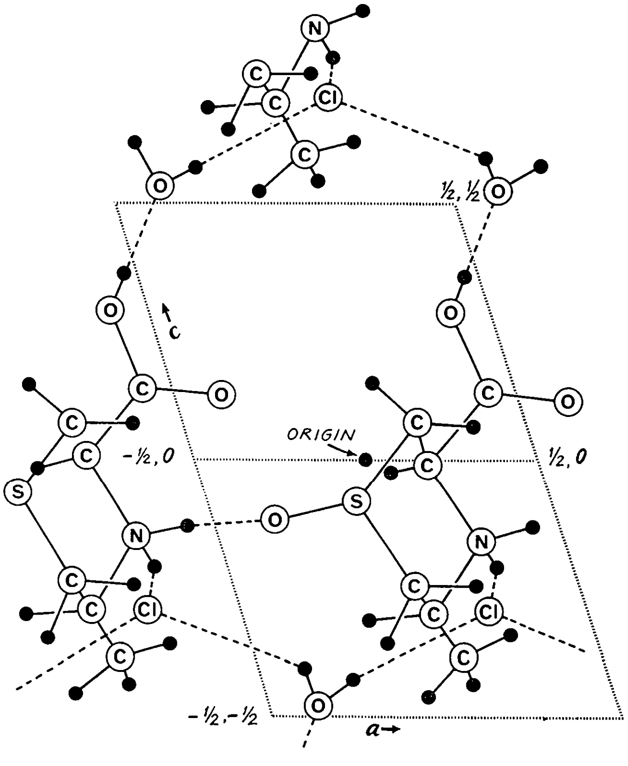

Fig. 2. The hydrogen bond network in crystalline cycloalliin hydrochloride monohydrate.

Table 2. *Thermal parameters* (Å²) *and standard deviations* (*in parentheses*)

	B_{11}*	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	2·54 (4)	2·45 (4)	3·44 (4)	−0·24 (4)	1·07 (3)	0·08 (4)
Cl	3·56 (5)	2·85 (4)	3·40 (4)	0·07 (4)	0·70 (4)	−0·00 (4)
N	2·65 (14)	2·27 (14)	2·30 (13)	0·21 (12)	0·75 (10)	−0·01 (11)
O(7)	2·32 (13)	4·32 (18)	5·61 (20)	−0·61 (12)	1·44 (13)	−0·01 (15)
O(9)	4·18 (16)	6·50 (24)	2·44 (12)	1·93 (17)	1·13 (12)	1·43 (15)
O(10)	3·61 (16)	5·86 (21)	3·86 (16)	1·87 (15)	1·51 (13)	1·41 (16)
O(aq.)	4·07 (18)	10·49 (39)	5·31 (21)	2·35 (22)	1·82 (16)	4·98 (24)
C(2)	2·66 (17)	2·94 (19)	2·69 (17)	0·38 (15)	0·41 (14)	−0·36 (15)
C(3)	2·62 (16)	2·53 (17)	2·16 (15)	0·02 (14)	0·67 (12)	0·12 (14)
C(5)	3·02 (17)	2·71 (18)	2·21 (16)	0·32 (15)	0·56 (13)	0·17 (14)
C(6)	3·12 (17)	2·61 (19)	2·91 (17)	0·35 (15)	0·95 (14)	0·47 (15)
C(8)	3·02 (18)	2·93 (19)	2·67 (17)	0·10 (16)	0·49 (14)	0·41 (16)
C(11)	5·92 (31)	4·11 (28)	2·35 (20)	1·12 (25)	1·34 (20)	0·28 (19)

	B†		*B*		*B*		*B*
H(1)	3(1)	H(5)	2 (1)	H(9)	2 (1)	H(13)	4 (2)
H(2)	1 (1)	H(6)	1 (1)	H(10)	2 (1)	H(14)	5 (3)
H(3)	2 (1)	H(7)	0 (1)	H(11)	3 (1)		
H(4)	1 (1)	H(8)	1 (1)	H(12)	1 (1)		

* Anisotropic values $B_{ij}=4\,\beta_{ij}/a^*_i a^*_j$ where a^*_i is the *i*th reciprocal cell length.

† Isotropic.

conformation of the methyl hydrogens is such that H(10) and H(6) are nearly in the eclipsed position. The cycloalliin isomer with the methyl group in the axial position has been prepared (Carson, 1956), but its crystal structure has not been determined. It would be interesting to know whether the methyl group influences the conformation of the six-membered ring. The peaks for the three methyl hydrogen atoms on the electron-density map are about as sharp as those for hydrogen atoms attached to other carbon atoms, indicating that the methyl group is essentially stationary in the crystal when observed at X-ray frequencies.

The molecules in the crystal are held together by a network of hydrogen bonds as shown in Fig. 2. The

Table 3. *Observed* (*FOBS*) *and calculated* (*FCAL*) *structure factors*

All values have been multiplied by 20

H,K= 0, 0

L	FOBS	FCAL
1	773	847
2	100	106
3	79	84
4	167	161
5	854	851
6	307	299
7	232	231
8	0	21
9	126	124
10	33	30

H,K= 0, 1

L	FOBS	FCAL
1	384	398
2	837	870
3	563	594
4	254	242
5	30	32
6	148	149
7	227	228
8	186	174
9	31	36
10	41	38

H,K= 0, 2

L	FOBS	FCAL
-0	382	343
1	582	616
2	313	305
3	317	314
4	243	249
5	364	355
6	344	341
7	230	239
8	169	170
9	124	124
10	59	54

H,K= 0, 3

L	FOBS	FCAL
1	1031	1119
2	299	292
3	450	457
4	349	347
5	266	261
6	509	512
7	150	142
8	228	208
9	43	46
10	41	49

H,K= 0, 4

L	FOBS	FCAL
-0	593	609
1	973	1018
2	326	332
3	291	286
4	416	423
5	141	135
6	322	327
7	282	276
8	64	72
9	78	73

H,K= 0, 5

L	FOBS	FCAL
1	853	870
2	466	465
3	382	368
4	402	414
5	251	239
6	121	122
7	113	111
8	73	70
9	68	61

H,K= 0, 6

L	FOBS	FCAL
-0	85	92
1	206	212
2	549	551
3	220	214
4	93	93
5	242	234
6	170	175
7	228	212
8	110	101
9	93	85

H,K= 0, 7

L	FOBS	FCAL
1	482	456
2	200	181
3	74	80
4	458	449
5	326	333
6	137	133
7	43	43
8	70	76
9	159	155

H,K= 0, 8

L	FOBS	FCAL
-0	315	292
1	91	99
2	302	307
3	106	104
4	111	112
5	169	177
6	163	163
7	218	219
8	61	58

H,K= 0, 9

L	FOBS	FCAL
1	370	378
2	140	142
3	121	111
4	315	317
5	237	231
6	104	120
7	80	85
8	107	103

H,K= 0, 10

L	FOBS	FCAL
-0	143	131
1	343	348
2	328	325
3	174	180
4	183	172
5	73	82
6	72	80
7	198	183
8	25	33

H,K= 0, 11

L	FOBS	FCAL
1	119	127
2	193	177
3	172	172
4	118	116
5	81	80
6	131	123
7	0	7

H,K= 0, 12

L	FOBS	FCAL
-0	311	298
1	130	132
2	166	163
3	69	77
4	107	105
5	139	135
6	134	129

H,K= 0, 13

L	FOBS	FCAL
1	109	119
2	111	114
3	170	181
4	66	74
5	33	55

H,K= 0, 14

L	FOBS	FCAL
-0	295	277
1	105	105
2	24	31
3	88	91
4	56	52

H,K= 0, 15

L	FOBS	FCAL
1	55	36
2	130	150
3	151	163

H,K= 1, 0

L	FOBS	FCAL
-10	0	29
-9	33	42
-8	357	377
-7	206	212
-6	41	38
-5	41	26
-4	355	327
-3	1085	1130
-2	526	521
-1	235	242
-0	381	400
1	605	611
2	344	333
3	100	99
4	123	121
5	143	125
6	384	392
7	52	53
8	0	8
9	66	59

H,K= 1, 1

L	FOBS	FCAL
-10	151	141
-9	68	75
-8	83	81
-7	191	211
-6	214	206
-5	600	579
-4	571	556
-3	187	190
-2	710	734
-1	730	744
-0	870	897
1	604	586
2	573	565
3	488	495
4	167	173
5	58	58
6	213	213
7	261	260
8	98	99
9	132	133

H,K= 1, 2

L	FOBS	FCAL
-10	15	23
-9	121	128
-8	192	190
-7	109	120
-6	201	204
-5	548	537
-4	702	703
-3	816	836
-2	719	743
-1	460	449
-0	1204	1220
1	840	842
2	773	773
3	703	677
4	270	255
5	186	182
6	365	370
7	121	117
8	134	139
9	69	64

H,K= 1, 3

L	FOBS	FCAL
-10	91	90
-9	130	128
-8	106	115
-7	265	283
-6	125	120
-5	342	335
-4	411	412
-3	438	449
-2	674	687
-1	380	360
-0	984	981
1	488	481
2	805	796
3	603	584
4	225	234
5	212	210
6	205	219
7	28	57
8	173	170
9	36	44

H,K= 1, 4

L	FOBS	FCAL
-10	118	126
-9	85	88
-8	167	139
-7	278	281
-6	359	354
-5	226	223
-4	308	311
-3	160	152
-2	326	326
-1	844	856
-0	415	421
1	810	799
2	387	373
3	101	81
4	180	164
5	106	105
6	270	265
7	215	209
8	150	152
9	14	23

H,K= 1, 5

L	FOBS	FCAL
-10	52	47
-9	89	87
-8	0	25
-7	241	218
-6	254	256
-5	271	275
-4	349	334
-3	285	281
-2	252	263
-1	316	302
-0	418	407
1	271	288
2	529	515
3	303	287
4	319	309
5	216	219
6	43	49
7	265	259
8	132	126
9	168	168

H,K= 1, 6

L	FOBS	FCAL
-9	86	86
-8	60	49
-7	62	56
-6	294	298
-5	200	200
-4	205	191
-3	233	225
-2	192	176
-1	502	497
-0	573	558
1	171	170
2	244	239
3	134	121
4	274	264
5	267	274
6	110	106
7	33	42
8	69	74

H,K= 1, 7

L	FOBS	FCAL
-9	106	108
-8	41	41
-7	127	158
-6	200	198
-5	159	150
-4	528	534
-3	340	340
-2	164	151
-1	77	82
-0	274	262
1	827	817
2	628	613
3	137	132
4	77	66
5	337	334
6	73	72
7	223	221
8	77	80

H,K= 1, 8

L	FOBS	FCAL
-9	44	46
-8	17	22
-7	136	136
-6	337	337
-5	99	103
-4	57	49
-3	75	78
-2	79	79
-1	579	566
-0	235	230
1	74	62
2	144	135
3	161	155
4	252	245
5	186	166
6	57	59
7	130	126
8	149	143

H,K= 1, 9

L	FOBS	FCAL
-8	57	57
-7	102	109
-6	131	138
-5	28	20
-4	234	237
-3	223	225
-2	75	72
-1	74	70
-0	251	231
1	221	244
2	317	317
3	110	105
4	169	166
5	178	168
6	0	9
7	123	117

H,K= 1, 10

L	FOBS	FCAL
-8	49	49
-7	94	93
-6	134	139
-5	202	202
-4	133	135
-3	125	126
-2	32	40
-1	363	366
-0	252	245
1	317	309
2	252	245
3	122	121
4	281	277
5	179	187
6	157	155
7	77	86

H,K= 1, 11

L	FOBS	FCAL
-7	63	76
-6	136	135
-5	216	220
-4	134	145
-3	161	164
-2	214	202
-1	149	146
-0	154	143
1	97	100
2	215	202
3	182	166
4	115	118
5	114	118
6	21	25

H,K= 1, 12

L	FOBS	FCAL
-7	103	116
-6	89	94
-5	108	103
-4	26	31
-3	177	166
-2	255	252
-1	188	202
-0	172	166
1	204	202
2	27	33
3	142	133
4	124	111
5	61	56
6	128	143

H,K= 1, 13

L	FOBS	FCAL
-6	25	23
-5	131	135
-4	115	117
-3	109	109
-2	200	188
-1	60	63
-0	208	212
1	124	118
2	48	52
3	184	178
4	107	101
5	23	22

H,K= 1, 14

L	FOBS	FCAL
-5	80	103
-4	57	58
-3	147	145
-2	140	134
-1	0	16
-0	168	170
1	172	176
2	79	85
3	87	106

H,K= 1, 15

L	FOBS	FCAL
-3	36	37
-2	123	134
-1	63	59
-0	53	80
1	42	52
2	11	14

H,K= 2, 0

L	FOBS	FCAL
-10	23	30
-9	80	90
-8	183	194
-7	347	357
-6	187	182
-5	124	118
-4	51	45
-3	580	554
-2	817	817
-1	335	314
-0	461	461
1	387	390
2	229	220
3	453	434
4	311	304
5	55	59
6	347	351
7	184	195
8	73	76

H,K= 2, 1

L	FOBS	FCAL
-10	188	192
-9	68	86
-8	151	151
-7	109	108
-6	188	174
-5	540	533
-4	638	621
-3	192	180
-2	418	416
-1	663	663
-0	427	410
1	575	555
2	477	461
3	86	79
4	371	365
5	173	180
6	171	164
7	97	103
8	0	5

H,K= 2, 2

L	FOBS	FCAL
-10	117	122
-9	68	78
-8	59	53
-7	199	189
-6	0	12
-5	357	350
-4	312	307
-3	209	180
-2	627	606
-1	498	491
-0	130	122
1	376	364
2	385	369
3	324	323
4	235	237
5	191	203
6	98	103
7	126	131
8	46	49

H,K= 2, 3

L	FOBS	FCAL
-10	117	111
-9	59	68
-8	129	131
-7	125	122
-6	172	178
-5	423	415
-4	77	77
-3	228	217
-2	139	150
-1	365	349
-0	634	612
1	448	437
2	444	436
3	335	337
4	273	269
5	77	84
6	185	184
7	67	69
8	78	88

H,K= 2, 4

L	FOBS	FCAL
-10	80	75
-9	171	180
-8	176	176
-7	272	271
-6	219	231
-5	55	58
-4	341	322
-3	455	448
-2	429	420
-1	254	238
-0	527	511
1	178	174
2	225	223
3	300	295
4	143	143
5	209	218
6	134	140
7	188	184
8	55	57

H,K= 2, 5

L	FOBS	FCAL
-10	42	34
-9	31	42
-8	80	90
-7	80	86
-6	341	336
-5	281	283
-4	567	563
-3	406	400
-2	40	32
-1	531	520
-0	224	207
1	558	544
2	317	305
3	254	247
4	207	209
5	43	49
6	167	158
7	170	158
8	209	209

H,K= 2, 6

L	FOBS	FCAL
-10	26	25
-9	170	165
-8	107	108
-7	150	148
-6	322	326
-5	349	349
-4	371	369
-3	307	307
-2	384	375
-1	410	391
-0	505	493
1	222	213
2	342	329
3	267	260
4	155	155
5	260	254
6	164	161
7	30	37
8	116	122

H,K= 2, 7

L	FOBS	FCAL
-9	55	51
-8	84	83
-7	123	118
-6	183	178
-5	37	44
-4	47	57
-3	302	290
-2	139	139
-1	240	244
-0	199	195
1	227	219
2	451	448
3	216	209
4	82	78
5	44	55
6	55	44
7	152	157

H,K= 2, 8

L	FOBS	FCAL
-9	154	158
-8	82	84
-7	50	58
-6	76	72
-5	198	205
-4	167	166
-3	245	246
-2	100	90
-1	289	285
-0	604	601
1	291	288
2	184	178
3	93	88
4	79	66
5	225	229
6	96	98
7	103	103

H,K= 2, 9

L	FOBS	FCAL
-8	90	92
-7	80	80
-6	187	185
-5	110	110
-4	206	195
-3	392	391
-2	66	61
-1	203	196
-0	169	172
1	365	367
2	398	393
3	198	183
4	95	91
5	64	66
6	96	108

H,K= 2, 10

L	FOBS	FCAL
-8	94	91
-7	122	127
-6	254	252
-5	87	91
-4	175	173
-3	255	249
-2	222	219
-1	225	234
-0	122	118
1	219	218
2	143	152
3	174	166
4	111	115
5	182	175
6	42	44

H,K= 2, 11

L	FOBS	FCAL
-7	50	45
-6	139	147
-5	239	232
-4	189	178
-3	194	189
-2	124	118
-1	198	199
-0	165	151
1	172	162
2	113	105
3	166	164
4	91	101
5	42	53

H,K= 2, 12

L	FOBS	FCAL
-6	42	49
-5	75	73
-4	90	92
-3	42	41
-2	214	206
-1	154	151
-0	153	160
1	94	100
2	66	60
3	174	174
4	144	141
5	82	90

H,K= 2, 13

L	FOBS	FCAL

Table 3 (*cont.*)

-6	35	48
-5	122	122
-4	134	138
-3	61	55
-2	48	44
-1	96	98
-0	88	93
1	229	240
2	100	99
3	90	84
4	79	94
H,K= 2, 14		
L	FOBS	FCAL
-4	40	37
-3	80	92
-2	213	227
-1	98	90
-0	50	50
1	65	69
2	13	26
H,K= 2, 15		
L	FOBS	FCAL
-2	18	29
-1	33	53
-0	72	98
H,K= 3, 0		
L	FOBS	FCAL
-10	131	134
-9	91	92
-8	130	147
-7	42	48
-6	232	237
-5	124	136
-4	47	35
-3	231	225
-2	137	137
-1	537	515
-0	301	299
1	230	232
2	120	103
3	219	219
4	240	245
5	143	147
6	26	31
7	36	36
H,K= 3, 1		
L	FOBS	FCAL
-10	0	22
-9	103	100
-8	149	143
-7	199	195
-6	63	64
-5	97	100
-4	594	588
-3	221	212
-2	167	162
-1	191	175
-0	199	194
1	622	615
2	552	545
3	82	84
4	0	12
5	123	133
6	104	114
7	207	200
H,K= 3, 2		
L	FOBS	FCAL
-10	113	110
-9	107	104
-8	112	112
-7	129	128
-6	150	158
-5	339	330
-4	437	418
-3	317	303
-2	314	328
-1	302	277
-0	60	51
1	286	275
2	384	383
3	195	193
4	294	310
5	118	121
6	96	100
7	75	75
H,K= 3, 3		
L	FOBS	FCAL
-10	94	93
-9	108	114
-8	75	77
-7	293	302
-6	146	162
-5	434	429
-4	236	225
-3	171	163
-2	463	446
-1	264	268
-0	244	256
1	210	201
2	217	207
3	221	220
4	148	151
5	96	114
6	138	140
7	120	109
H,K= 3, 4		
L	FOBS	FCAL
-10	120	126
-9	138	139
-8	79	77
-7	200	197
-6	223	221
-5	125	135
-4	210	210
-3	331	324
-2	259	252
-1	538	511
-0	393	367
1	320	315
2	236	242
3	150	149
4	262	256
5	99	100
6	138	149
7	69	68
H,K= 3, 5		
L	FOBS	FCAL
-10	55	57
-9	132	132
-8	42	53
-7	71	73
-6	102	90
-5	233	241
-4	193	186
-3	24	21
-2	269	261
-1	126	130
-0	446	428
1	274	253
2	119	121
3	255	261
4	34	35
5	148	139
6	35	39
7	40	39
H,K= 3, 6		
L	FOBS	FCAL
-9	160	154
-8	247	247
-7	80	88
-6	98	104
-5	183	182
-4	94	106
-3	481	477
-2	271	264
-1	143	137
-0	142	139
1	193	199
2	263	261
3	301	299
4	34	41
5	79	80
6	188	188
H,K= 3, 7		
L	FOBS	FCAL
-9	34	39
-8	43	47
-7	142	136
-6	361	345
-5	209	205
-4	77	90
-3	97	99
-2	44	59
-1	333	328
-0	280	273
1	140	149
2	0	17
3	88	84
4	54	54
5	188	194
6	36	36
H,K= 3, 8		
L	FOBS	FCAL
-9	80	88
-8	214	211
-7	66	66
-6	67	66
-5	28	27
-4	222	218
-3	512	526
-2	291	292
-1	83	90
-0	193	195
1	149	141
2	214	209
3	187	195
4	59	60
5	100	98
6	105	108
H,K= 3, 9		
L	FOBS	FCAL
-8	46	50
-7	110	120
-6	161	154
-5	272	261
-4	76	82
-3	48	55
-2	236	226
-1	150	148
-0	409	402
1	135	124
2	70	70
3	171	183
4	43	42
5	118	117
H,K= 3, 10		
L	FOBS	FCAL
-8	72	86
-7	44	38
-6	47	45
-5	123	112
-4	98	108
-3	131	133
-2	123	126
-1	71	71
-0	102	90
1	27	41
2	141	132
3	141	146
4	87	84
5	62	58
H,K= 3, 11		
L	FOBS	FCAL
-7	70	78
-6	143	140
-5	119	137
-4	133	132
-3	62	61
-2	214	223
-1	130	130
-0	165	175
1	165	173
2	112	114
3	200	195
4	84	92
H,K= 3, 12		
L	FOBS	FCAL
-6	107	119
-5	84	89
-4	158	158
-3	126	122
-2	118	109
-1	175	179
-0	31	37
1	161	171
2	49	40
3	40	35
H,K= 3, 13		
L	FOBS	FCAL
-5	81	86
-4	174	178
-3	57	62
-2	93	101
-1	42	47
-0	85	89
1	137	145
2	118	140
H,K= 3, 14		
L	FOBS	FCAL
-3	19	13
-2	56	69
-1	96	119
-0	31	41
H,K= 4, 0		
L	FOBS	FCAL
-10	79	84
-9	200	189
-8	153	148
-7	0	29
-6	0	12
-5	210	221
-4	276	277
-3	395	391
-2	35	40
-1	200	198
-0	0	7
1	74	80
2	223	230
3	0	12
4	74	79
5	75	66
6	54	56
H,K= 4, 1		
L	FOBS	FCAL
-10	36	40
-9	45	48
-8	62	62
-7	287	274
-6	303	297
-5	56	55
-4	148	147
-3	193	186
-2	274	279
-1	519	510
-0	222	222
1	294	296
2	369	374
3	56	57
4	222	226
5	72	77
6	42	43
H,K= 4, 2		
L	FOBS	FCAL
-10	47	44
-9	123	133
-8	26	31
-7	109	105
-6	226	219
-5	187	195
-4	345	339
-3	341	342
-2	253	268
-1	200	200
-0	192	175
1	264	266
2	313	321
3	206	208
4	94	97
5	131	138
6	0	21
H,K= 4, 3		
L	FOBS	FCAL
-10	22	14
-9	49	49
-8	135	128
-7	126	115
-6	153	134
-5	291	284
-4	252	252
-3	178	167
-2	160	144
-1	192	194
-0	221	221
1	132	142
2	176	181
3	76	78
4	124	125
5	86	79
6	62	68
H,K= 4, 4		
L	FOBS	FCAL
-9	164	161
-8	112	113
-7	166	163
-6	133	128
-5	163	173
-4	321	315
-3	161	163
-2	336	352
-1	120	123
-0	267	264
1	116	127
2	28	38
3	184	192
4	140	134
5	135	135
6	0	4
H,K= 4, 5		
L	FOBS	FCAL
-9	49	47
-8	164	165
-7	125	120
-6	184	180
-5	278	262
-4	154	152
-3	243	251
-2	127	133
-1	125	125
-0	263	266
1	314	316
2	130	131
3	47	51
4	25	38
5	93	89
H,K= 4, 6		
L	FOBS	FCAL
-9	63	67
-8	85	80
-7	58	56
-6	137	134
-5	149	154
-4	89	90
-3	272	261
-2	267	268
-1	90	86
-0	55	53
1	159	155
2	126	126
3	302	303
4	111	111
5	61	68
H,K= 4, 7		
L	FOBS	FCAL
-8	126	131
-7	36	27
-6	0	33
-5	195	196
-4	198	191
-3	129	123
-2	85	80
-1	59	70
-0	100	97
1	191	182
2	27	41
3	48	64
4	52	44
5	14	11
H,K= 4, 8		
L	FOBS	FCAL
-8	99	106
-7	77	79
-6	118	120
-5	173	175
-4	51	58
-3	212	199
-2	229	222
-1	73	75
-0	182	193
1	83	96
2	45	51
3	188	187
4	84	87
H,K= 4, 9		
L	FOBS	FCAL
-7	94	104
-6	78	77
-5	157	151
-4	79	83
-3	174	173
-2	94	100
-1	66	73
-0	162	164
1	145	153
2	35	40
3	106	102
4	91	88
H,K= 4, 10		
L	FOBS	FCAL
-7	67	87
-6	71	70
-5	114	109
-4	143	138
-3	93	92
-2	151	144
-1	55	62
-0	103	107
1	51	54
2	99	98
3	105	106
H,K= 4, 11		
L	FOBS	FCAL
-6	49	63
-5	139	150
-4	96	95
-3	60	71
-2	63	61
-1	97	102
-0	201	207
1	161	164
2	133	143
H,K= 4, 12		
L	FOBS	FCAL
-4	108	140
-3	84	92
-2	110	120
-1	43	47
-0	61	68
1	33	53
H,K= 5, 0		
L	FOBS	FCAL
-9	74	76
-8	130	129
-7	64	64
-6	171	167
-5	0	10
-4	182	183
-3	396	398
-2	146	153
-1	160	166
-0	71	82
1	100	107
2	137	129
3	130	142
4	52	62
H,K= 5, 1		
L	FOBS	FCAL
-9	84	89
-8	94	91
-7	144	138
-6	224	225
-5	92	93
-4	163	157
-3	168	167
-2	224	223
-1	259	259
-0	224	233
1	116	121
2	72	72
3	24	34
4	83	98
H,K= 5, 2		
L	FOBS	FCAL
-9	138	143
-8	110	102
-7	55	62
-6	138	145
-5	236	238
-4	176	170
-3	192	182
-2	0	2
-1	157	156
-0	130	147
1	101	110
2	218	218
3	94	94
4	18	7
H,K= 5, 3		
L	FOBS	FCAL
-9	90	118
-8	152	147
-7	130	134
-6	156	154
-5	121	118
-4	151	149
-3	150	154
-2	200	198
-1	219	215
-0	172	168
1	167	180
2	63	77
3	119	127
4	106	113
H,K= 5, 4		
L	FOBS	FCAL
-8	39	40
-7	106	102
-6	81	86
-5	66	70
-4	157	159
-3	252	249
-2	94	81
-1	87	98
-0	79	95
1	97	92
2	154	155
3	124	120
4	117	129
H,K= 5, 5		
L	FOBS	FCAL
-8	113	112
-7	142	147
-6	68	65
-5	75	76
-4	156	154
-3	128	124
-2	236	231
-1	96	94
-0	84	79
1	129	136
2	98	101
3	76	77
H,K= 5, 6		
L	FOBS	FCAL
-8	34	42
-7	0	9
-6	76	78
-5	276	275
-4	219	209
-3	76	68
-2	120	112
-1	73	80
-0	163	158
1	97	106
2	104	107
3	118	123
H,K= 5, 7		
L	FOBS	FCAL
-7	119	127
-6	32	36
-5	0	3
-4	103	97
-3	0	20
-2	200	204
-1	63	61
-0	73	68
1	124	127
2	105	106
H,K= 5, 8		
L	FOBS	FCAL
-7	33	59
-6	32	30
-5	86	92
-4	76	83
-3	58	55
-2	138	136
-1	106	103
-0	88	85
1	147	145
2	103	111
H,K= 5, 9		
L	FOBS	FCAL
-6	15	13
-5	41	39
-4	106	117
-3	71	78
-2	151	150
-1	87	89
-0	49	55
1	145	149
H,K= 5, 10		
L	FOBS	FCAL
-4	141	154
-3	83	90
-2	81	90
-1	109	108
-0	20	34
H,K= 6, 0		
L	FOBS	FCAL
-7	39	38
-6	138	141
-5	158	158
-4	0	15
-3	107	105
-2	138	136
-1	101	106
-0	129	128
1	20	13
H,K= 6, 1		
L	FOBS	FCAL
-7	34	37
-6	0	10
-5	0	16
-4	53	65
-3	214	224
-2	43	63
-1	48	52
-0	68	64
1	52	58
H,K= 6, 2		
L	FOBS	FCAL
-7	37	44
-6	168	168
-5	78	76
-4	25	29
-3	90	92
-2	89	90
-1	75	77
-0	70	72
1	19	34
H,K= 6, 3		
L	FOBS	FCAL
-7	74	85
-6	29	23
-5	121	129
-4	122	126
-3	121	126
-2	128	127
-1	71	72
-0	135	135
1	96	104
H,K= 6, 4		
L	FOBS	FCAL
-6	81	81
-5	79	77
-4	148	154
-3	108	109
-2	126	130
-1	54	52
-0	126	131
1	86	99
H,K= 6, 5		
L	FOBS	FCAL
-6	71	87
-5	130	136
-4	15	27
-3	41	46
-2	144	151
-1	123	125
-0	92	96
H,K= 6, 6		
L	FOBS	FCAL
-5	61	84
-4	108	123
-3	77	83
-2	0	12
-1	39	51
H,K= 6, 7		
L	FOBS	FCAL
-4	42	46
-3	22	32
-2	134	149

water molecule is hydrogen-bonded to one carboxyl group and two chloride ions. The intermolecular N–O(7) distance of 2·692 Å and the intramolecular N–O(10) distance of 2·687 Å are nearly the same, but apparently only O(7) forms a hydrogen bond with N. This is evident from the fact that H(5) is 2·0 Å from O(7), but is 2·6 Å from O(10). Any attraction that exists between N and O(10) must result from the formal positive charge on N and the negative charge on O(10) which results from resonance in the carboxyl group.

The O(9)–H---O(aq.) distance of 2·541 Å is indicative of a strong hydrogen bond. The O(aq.)–H---Cl distances (3·156 Å and 3·140 Å) and the N–H---Cl distance (3·108 Å) are those to be expected for hydrogen bonding between chloride ion and oxygen and nitrogen respectively.

Table 4. *Interatomic distances and standard deviations* (*in parentheses*)

S——O(7)	1·492 (5) Å	C(5)—C(11)	1·513 (7) Å
S——C(2)	1·802 (6)	N——C(3)	1·484 (6)
S——C(6)	1·804 (6)	N——C(5)	1·499 (6)
C(2)—C(3)	1·518 (7)	C(8)—O(9)	1·311 (6)
C(3)—C(8)	1·521 (6)	C(8)—O(10)	1·195 (6)
C(6)—C(5)	1·515 (7)		
C(2)—H(1)	1·08 (6)	O(9)—H(9)	0·94 (5)
C(2)—H(2)	0·93 (5)	N——H(4)	0·93 (5)
C(3)—H(3)	1·08 (5)	N——H(5)	0·66 (6)
C(5)—H(6)	1·00 (5)	O(aq.)-H(13)	0·66 (7)
C(6)—H(7)	1·00 (4)	O(aq.)-H(14)	0·51 (9)
C(6)—H(8)	0·91 (6)	Cl——H(4)	2·18 (5)
C(11)-H(10)	0·85 (6)	Cl——H(14)	2·72 (9)
C(11)-H(11)	1·14 (6)	Cl——H(13)	2·58 (7)
C(11)-H(12)	0·99 (6)	Cl——H(11)	2·79 (6)
		Cl——H(2)	2·73 (5)
Cl---H-N	3·108 (6)	O(aq.)---H-O(9)	2·541 (9)
Cl---H-O(aq.)	3·156 (8)	O(7)---H-N	2·692 (6)
Cl---H-O(aq.)	3·140 (8)	O(10)---H-N	2·687 (6)

Table 5. *Interatomic angles and standard deviations* (*in parentheses*)

C(2)—S——C(6)	96·9 (3)°	C(2)—C(3)—C(8)	109·8 (4)°
O(7)—S——C(2)	107·1 (3)	N——C(5)—C(6)	110·1 (4)
O(7)—S——C(6)	104·7 (3)	N——C(5)—C(11)	108·6 (4)
C(3)—N——C(5)	115·1 (4)	C(3)—C(8)—O(9)	110·8 (4)
S——C(2)—C(3)	113·0 (3)	C(3)—C(8)—O(10)	123·7 (4)
C(2)—C(3)—N	112·1 (4)	O(9)—C(8)—O(10)	125·4 (5)
N——C(5)—H(6)	103 (3)	C(3)—C(2)—H(1)	112 (3)
C(3)—N——H(4)	111 (3)	C(3)—C(2)—H(2)	116 (3)
C(3)—N——H(5)	106 (4)	C(2)—C(3)—H(3)	110 (3)
C(5)—N——H(4)	105 (3)	C(6)—C(5)—H(6)	114 (3)
C(5)—N——H(5)	108 (5)	C(5)—C(6)—H(7)	109 (2)
C(8)—O(9)—H(9)	114 (3)	C(5)—C(6)—H(8)	122 (4)
H(13)-O(aq.)-H(14)	122 (13)	H(10)-C(11)-H(11)	112 (5)
H(1)—C(2)—H(2)	101 (4)	H(10)-C(11)-H(12)	95 (5)
H(7)—C(6)—H(8)	98 (4)	H(11)-C(11)-H(12)	130 (4)

Although the accuracy of the hydrogen parameters is considerably less than for the heavier atoms as shown by the standard deviations in Table 1, the C–H distances cluster around the values usually reported for this bond. The N–H(4) distance of 0·93 Å indicates unequivocally that H(4) is covalently bonded to nitrogen and that chlorine occurs in the structure as the negative ion.

The N–H(5) distance of 0·70 Å and the O(aq.)–H distances of 0·60 Å and 0·54 Å are clearly too short. In the case of the water molecule the short O–H distances may result from the large vibration amplitude of the water oxygen atom, as indicated in Table 2 by the comparatively large values of the thermal parameters for this atom.

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References

Abrahams, S. C. (1956). *Quart. Rev. Chem. Soc. London*, **10**, 407.

Cairns, T., Eglington, G. & Gibson, D. C. (1964). *Spectrochim. Acta*, **20**, 159.

Carson, J. F. (1965). Private communication.

Cheung, K. K., Kjaer, A. & Sim, G. A. (1965). *Chem. Comm.* No. 6, 100.

Fleischer, E. B., Axelrod, M., Green, M. & Mislow, K. (1964). *J. Amer. Chem. Soc.* **86**, 3395.

Gantzel, P. K., Sparks, R. A., & Trueblood, K. N. (1961). Private communication with A. Zalkin.

Hine, R. (1962). *Acta Cryst.* **15**, 635.

Johnson, C. R. & McCants, D., Jr. (1964). *J. Amer. Chem. Soc.* **86**, 2935.

Jones, F. T., Lee, K. S., Black, D. R. & Palmer, K. J. (1965). *Microscope and Crystal Front*, **14**, 379.

Martin, J. C. & Uebel, J. J. (1964). *J. Amer. Chem. Soc.* **86**, 2936.

Mathieson, A. McL. (1956). *Acta Cryst.* **9**, 317.

Shearer, H. M. M. (1959). *J. Chem. Soc. p.* 1394.

Templeton, D. H. (1962). *International Tables for X-Ray Crystallography*. Vol. 3, p. 214, Birmingham: Kynoch Press.

Virtanen, A. I. & Matikkala, E. J. (1959). *Acta Chem. Scand.* **13**, 623.