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Crystal and Molecular Structure of Thiocarbohydrazide Dihydrochloride Dihydrate

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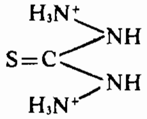
The crystals of thiocarbohydrazide dihydrochloride dihydrate, $SC(NH-NH_3)_2Cl_2 . 2H_2O$ are monoclinic, space group C2/c. The structure has been determined from three-dimensional data measured by automatic diffractometer. The final agreement factor was R = 3.8% with hydrogen atoms contribution. In the crystal structure, the cation



possess a binary symmetry axis. Its trans, trans, *conformation is different from the* cis, trans *conformation of the neutral molecules. Other relevant differences between diprotonated and neutral form concern the displacement of the terminal groups $-\overset{+}{N}H_3$ with respect to the plane of the thioureide group, N–CS–N, and the distribution of the single-double bond character between the bonds C–N and S–C. In the cation, in fact, the double bond character of S–C = 1.645(3) Å is more, and that of C–N(1) = 1.363(5) Å less pronounced than in the neutral molecule. These results agree with the behaviour of thiocarbohydrazide in acidic or in alkaline solutions.*

The anion-cation, water-anion and water-cations interactions correspond to hydrogen bonds.

Introduction

As part of researches on the properties of thiocarbohydrazide in the crystal state[1] and in solution[2,3] we have undertaken the study of the crystal structure of thiocarbohydrazide dihydrochloride dihydrate.

Experimental Section

Preparation. Prismatic crystals are obtained from aqueous solutions of thiocarbohydrazide and hydrochloric acid, at pH ~0.5.

Crystal Data. Compound: thiocarbohydrazide dihydrochloride dihydrate, $SC(NH-NH_3)_2Cl_2 . 2H_2O$, F. W. 215.11.

Crystal class: Monoclinic, prismatic.

Unit cell (radiation MoKα, $\lambda = 0.71069$ Å):

$a = 9.07(1)$, $b = 8.48(1)$, $c = 11.16(1)$ Å;
$\beta = 97.8(2)°$, $V = 850.4$ Å^3, $Z = 4$;
$D_x = 1.68$, $D_m = 1.68$ g.cm^{-3};
$\mu(MoK\alpha) = 9.53$ cm^{-1}.

Space group: $C2/c$ (No. 15, C_{2h}^6) from systematic absences and structure determination.

Intensities. Intensities of 894 (out of 967 possible) reflections have been measured by an automatic diffractometer Siemens «on line» (MoKα, $2\theta_{max} = 55°$).

Calculations. No absorption correction has been applied. The atomic form factors of Cromer and Mann[4] have been used. The structure has been solved by Patterson and Fourier methods and refined by differential syntheses. The hydrogen atoms have been identified in the difference map but their coordinates not refined. Anisotropic, for heavy atoms, and iso-

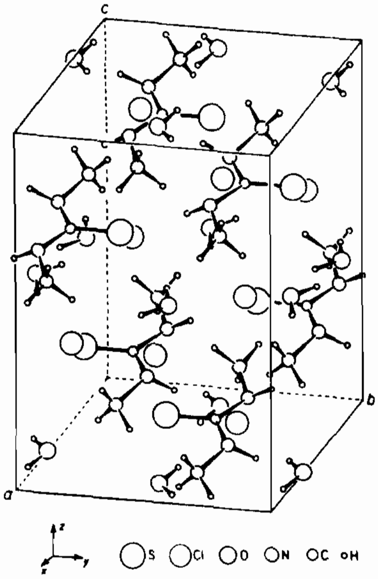


Figure 1. Clinographic projection of the structure of thiocarbohydrazide dihydrochloride dihydrate.

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(1) A. Braibanti, A. Tiripicchio, and M. Tiripicchio Camellini, *Acta Cryst. B 25,* 2286 (1969).

(2) A. Braibanti, E. Leporati, F. Dallavalle, and M. A. Pellinghelli, *Inorg. Chim. Acta, 2,* 449 (1968).

(3) A. Braibanti, F. Dallavalle, and E. Leporati, *Inorg. Chim. Acta, 3,* 459 (1969).

(4) D. T. Cromer and J. B. Mann, *Acta Cryst., A 24,* 321 (1968).

tropic, for hydrogen atoms, temperature factors have been introduced. Final conventional factor for observed reflections was R=3.8% (R=4.6% without hydrogen atoms contributions). All the calculations have been performed on the computer Olivetti Elea 6001/S of Centro di Calcolo Elettronico of the University of Parma.

The results of the structure determination are quoted in Tables I-VI.

Table I. Fractional atomic coordinates x 10^4 (with e.s.d's).

	x	y	z
Cl	4541(1)	—2992(1)	4119(1)
S	5000	0851(1)	2500
O_w	2814(2)	0178(2)	4792(2)
N(1)	3880(3)	3701(2)	2823(3)
N(2)	2674(2)	2924(2)	3259(2)
C	5000	2791(2)	2500
H(1.1)	4109	4719	3198
H(2.1)	2311	3575	3817
H(2.2)	1972	2644	2645
H(2.3)	2972	2104	3833
H(5)	3500	—0586	4717
H(6)	1783	—0212	4961

Table II. Thermal parameters (Å^2).

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	1.838	1.836	2.368	—0.090	0.236	—0.013
S	1.882	1.263	2.754	0.000	0.663	0.000
O_w	2.076	2.071	2.569	0.051	0.521	—0.007
N(1)	1.497	1.456	2.435	0.049	0.415	—0.166
N(2)	1.528	1.824	2.160	0.081	0.361	—0.047
C	1.533	1.408	1.166	0.000	0.022	0.000

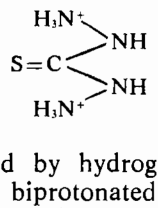
In the last cycle for all the atoms the average shift $|\Delta B_{ij}|_{av}$, and the maximum shift $|\Delta B_{ji}|_{max}$, were

$$|\Delta B_{ij}|_{av} = 0.019$$
$$|\Delta B_{ij}|_{max} = 0.088$$

	B		B
H(1.1)	2.25	H(2.3)	2.25
H(2.1)	2.25	H(5)	2.25
H(2.2)	2.25	H(6)	2.25

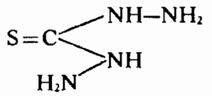
Discussion

The structure (Figure 1) consists of cations



$$S{=}C\begin{matrix}\diagup NH-H_3N^+ \\ \diagdown NH-H_3N^+\end{matrix}$$

and Cl^- anions, ioined by hydrogen bonds to the water molecules. The biprotonated cation lies on a binary axis passing through the bond S–C. Both groups $-NH-\overset{+}{N}H_3$ (Figure 2) are bent, with $-\overset{+}{N}H_3$ toward the sulphur atom; its *cis, cis* conformation is therefore different from the *cis, trans* conformation of the neutral[1] or chelate[5] molecule



$$S{=}C\begin{matrix}\diagup NH-NH_2 \\ \diagdown NH-H_2N\end{matrix}$$

There are significant differences in bond lengths and angles between neutral and diprotonated molecules. In the cation form, the atoms N(2) of the $-\overset{+}{N}H_3$ groups are on opposite sides (±0.09 Å) of the plane passing through the thioureide group, N–CS–N whereas both terminal nitrogen atoms of the neutral molecule[1] are displaced to the same side, *i.e.* –0.062 Å and –0.120 Å with respect to the plane of the thioureide group. The atoms H(1.1) are out of the N–CS–N plane, being 350.6° the sum of the angles around N(1) against 360° in the thiocarbohydrazide molecule; N(1) is not completely in sp^2 configuration. Even if angles involving hydrogen atoms are not taken into account, the angle C–N(1)–N(2)=117.8(2)° is significantly different from the corresponding angle in the neutral molecule, 122.4(7)°. The main differences, however, are in the carbon-sulphur and carbon-nitrogen bonds, with C–S=1.645(3) Å and C–N(1)=1.363(5) Å against values in the neutral molecule

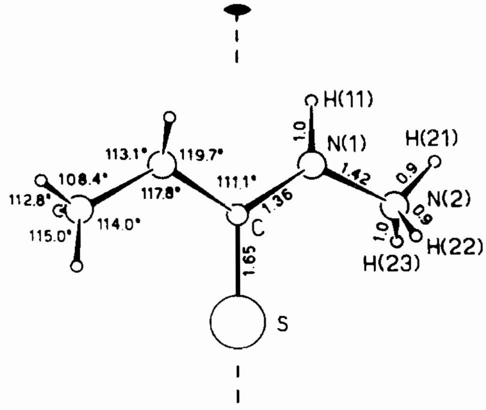


Figure 2. Cation $SC(NH-NH_3)^{2+}$.

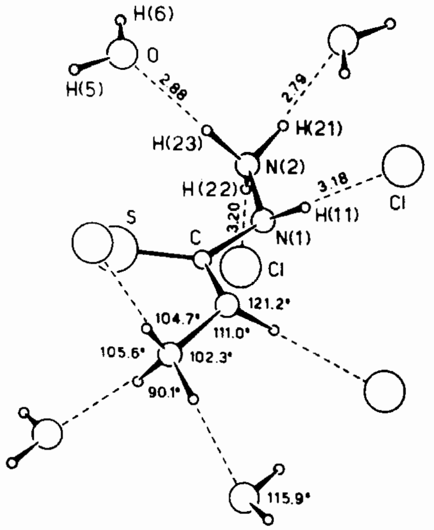


Figure 3. Intermolecular interactions.

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(5) F. Bigoli, A. Braibanti, A. M. Manotti Lanfredi, A. Tiripicchio, and M. Tiripicchio Camellini, *Inorg. Chim. Acta*, 5, 392 (1971).

Table III. Observed and calculated structure factors.
= after F_o values indicates unobserved reflections.

h	k	l	$10F_o$	$10F_c$
0	2	0	698	-734
0	4	0	354	386
0	6	0	52	44
0	8	0	281	-262
0	10	0	463	455
0	2	1	60	-53
0	4	1	288	-255
0	6	1	237	-227
0	8	1	235	218
0	10	1	255	260
0	0	2	382	-361
0	2	2	341	339
0	4	2	648	671
0	6	2	497	499
0	8	2	48	-54
0	10	2	44	37
0	2	3	576	-555
0	4	3	991	1036
0	6	3	527	-518
0	8	3	53	62
0	10	3	257	-260
0	0	4	554	543
0	2	4	868	928
0	4	4	178	-157
0	6	4	237	-233
0	8	4	233	234
0	10	4	63	-65
0	2	5	406	-405
0	4	5	52	-39
0	6	5	298	-297
0	8	5	209	205
0	10	5	121	118
0	0	6	678	-691
0	2	6	521	527
0	4	6	189	184
0	6	6	196	202
0	8	6	270	271
0	2	7	453	438
0	4	7	232	-225
0	6	7	259	259
0	8	7	326	-323
0	0	8	154	162
0	2	8	349	320
0	6	8	76	-72
0	6	4	181	-182
0	8	8	52	56
0	2	9	10-	10
0	4	9	531	-514
0	6	9	259	264
0	8	9	93	-99
0	0	10	132	132
0	2	10	216	-207
0	4	10	105	104
0	6	10	219	224
0	2	11	159	149
0	4	11	81	78
0	4	11	106	-106
0	0	12	460	434
0	2	12	254	-235
0	4	12	127	124
0	6	12	61	-61
0	2	13	208	-201
0	4	13	8-	-7
0	0	14	111	-115
0	2	14	8-	9
1	1	0	98	117
1	3	0	980	-1044
1	5	0	855	863
1	7	0	158	-154
1	9	0	156	170
1	1	1	299	300
1	1	-1	108	-96
1	3	1	844	885
1	3	-1	656	-628
1	5	1	173	168
1	5	-1	36	28
1	7	1	277	-277
1	7	-1	379	371
1	9	1	160	160
1	9	-1	114	108
1	1	2	49	41
1	1	-2	366	372
1	3	2	413	392
1	3	-2	664	-675
1	5	2	271	-252
1	5	-2	189	183
1	7	2	225	-213
1	7	-2	585	-569
1	9	2	88	-93
1	9	-2	62	56
1	1	3	1834	-1942
1	1	-3	942	1004
1	3	3	279	241
1	3	-3	180	164
1	5	3	22-	18
1	5	-3	200	190
1	7	3	22-	35
1	7	-3	116	116
1	9	3	509	497
1	9	-3	340	-332
1	1	4	68	-54
1	1	-4	768	-827
1	3	4	172	164
1	3	-4	105	106
1	5	4	23-	-21
1	5	-4	191	-185
1	7	4	437	426
1	7	-4	316	306
1	9	4	35	42
1	9	-4	91	-87
1	1	5	571	535
1	1	-5	435	404
1	3	5	370	346
1	3	-5	556	-525
1	5	5	136	131
1	5	-5	61	-60
1	7	5	108	-116
1	7	-5	340	334
1	9	5	45	-40
1	9	-5	10-	9
1	1	6	95	112
1	1	-6	134	-113
1	3	6	715	704
1	3	-6	216	213
1	5	6	538	-533
1	5	-6	806	-785
1	7	6	145	152
1	7	-6	113	115
1	9	6	120	-126
1	9	-6	114	-116
1	1	7	246	219
1	1	-7	62	-65
1	3	7	507	-487
1	3	-7	282	281
1	5	7	7-	7
1	5	-7	204	202
1	7	7	343	349
1	7	-7	138	-136
1	9	7	78	-79
1	9	-7	52	-52
1	1	8	8-	-8
1	1	-8	516	-519
1	3	8	88	88
1	3	-8	44	44
1	5	8	164	157
1	5	-8	5-	0
1	7	8	202	208
1	7	-8	68	73
1	9	-8	44	-46
1	1	9	459	435
1	1	-9	572	-583
1	3	9	54	43
1	3	-9	233	228
1	5	9	76	74
1	5	-9	186	-182
1	7	9	29	28
1	7	-9	103	-101
1	1	10	359	346
1	1	-10	99	108
1	3	10	186	-171
1	3	-10	214	-223
1	5	10	256	258
1	5	-10	211	-203
1	7	10	252	-253
1	7	-10	89	-89
1	1	11	80	-80
1	1	-11	8-	-8
1	3	11	112	-108
1	3	-11	71	83
1	5	11	50	-54
1	5	-11	144	144
1	7	-11	73	-75
1	1	12	37	39
1	1	-12	101	-126
1	3	12	81	-83
1	3	-12	238	-273
1	5	12	299	306
1	5	-12	357	362
1	1	13	133	-128
1	1	-13	67	67
1	3	13	159	159
1	3	-13	94	-102
1	1	14	105	107
1	1	-14	68	74
2	0	0	638	640
2	2	0	662	-652
2	4	0	382	-364
2	6	0	327	-316
2	8	0	340	-338
2	10	0	240	237
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2	4	-2	144	143
2	6	2	110	105
2	6	-2	317	299
2	8	2	28	-30
2	8	-2	253	-244
2	10	2	127	-121
2	10	-2	134	142
2	2	3	343	-316
2	2	-3	110	-101
2	4	3	791	796
2	4	-3	831	-886
2	6	3	343	-334
2	6	-3	429	406
2	8	3	10-	17
2	8	-3	103	-110
2	10	3	204	-208
2	10	-3	82	77
2	0	4	226	-222
2	0	-4	52	73
2	2	4	176	167
2	2	-4	190	-184
2	4	4	624	-616
2	4	-4	158	-155
2	6	4	450	-450
2	6	-4	384	-383
2	8	4	166	170
2	8	-4	167	-164
2	10	4	150	-155
2	10	-4	91	80
2	2	5	191	180
2	2	-5	650	664
2	4	5	506	-483
2	4	-5	163	-158
2	6	5	156	150
2	6	-5	57	48
2	8	5	50	47
2	8	-5	291	-293
2	10	5	230	230
2	10	-5	146	-147
2	0	6	1368	-1428
2	0	-6	1014	-1098
2	2	6	261	205
2	2	6	476	460
2	4	6	116	-105
2	4	-6	356	-350
2	6	6	14-	18
2	6	-6	108	104
2	8	6	153	149
2	8	-6	377	379
2	2	7	261	253
2	2	-7	379	-379
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2	4	-7	338	-339
2	6	7	311	305
2	6	-7	139	137
2	8	7	180	-180
2	8	-7	25	-25
2	0	8	482	440
2	0	-8	133	-133
2	2	8	271	-264
2	2	-8	211	225
2	4	8	182	-180
2	4	-8	19-	-19
2	6	8	179	-188
2	6	-8	259	-291
2	8	8	92	-89
2	8	-8	17-	-13
2	2	9	155	136
2	2	-9	28	-31
2	4	9	393	-373
2	4	-9	500	506
2	6	9	197	200
2	6	-9	515	-510
2	8	9	8-	4
2	8	-9	60	58
2	0	10	30	28
2	0	-10	43	-47
2	2	10	389	-369
2	2	-10	71	-83
2	4	10	159	162
2	4	-10	10-	-8
2	6	10	153	157
2	6	-10	183	177
2	2	11	21-	21
2	2	-11	243	-340
2	4	11	191	196
2	4	-11	36	39
2	6	11	10-	-8
2	6	-11	114	-121
2	0	12	268	236
2	0	-12	336	374
2	2	12	85	-84
2	2	-12	88	-120
2	4	12	55	-58
2	4	-12	79	94
2	6	-12	47	-44
2	2	13	178	-179
2	2	-13	148	174
2	4	-13	33	-35
2	0	-14	91	115
2	2	-14	116	-120
3	1	0	52	-64
3	3	0	121	-136
3	5	0	812	796
3	7	0	63	-71
3	9	0	76	77
3	1	1	865	-913
3	1	-1	612	-634
3	3	1	662	686
3	3	-1	47	-51
3	5	1	98	89
3	5	-1	391	-385
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3	7	-1	38	-40
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3	9	-1	280	269
3	1	2	474	441
3	1	-2	1001	1090
3	3	2	155	118
3	3	-2	334	-332
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3	5	-2	196	183
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3	7	-2	260	-262
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3	1	3	532	-511
3	1	-3	972	1021
3	3	3	256	-237
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3	5	-3	296	275
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3	7	-3	55	51
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3	1	-4	80	-104
3	3	4	558	551
3	3	-4	82	80
3	5	4	351	-356
3	5	-4	792	777
3	7	4	520	522
3	7	-4	73	-78
3	9	4	99	-102
3	9	-4	99	96
3	1	5	526	509
3	1	-5	313	309
3	3	5	61	64
3	3	-5	296	-314
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3	5	-5	339	-333
3	7	5	116	-125
3	7	-5	225	217
3	9	5	259	-253
3	9	-5	17-	15
3	1	6	21-	-24
3	1	-6	492	453
3	3	6	286	269
3	3	-6	515	499
3	5	6	407	-413
3	5	-6	626	-625
3	7	6	15-	-22
3	7	-6	325	324
3	9	6	82	-88
3	9	-6	39	-46
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3	1	-7	184	172
3	3	7	474	-469
3	3	-7	25	25
3	5	7	98	-96
3	5	-7	232	214
3	7	7	210	224
3	7	-7	46	-42
3	9	-7	227	-221
3	1	8	36	-44
3	1	-8	229	-233
3	3	8	398	-394
3	3	-8	517	531
3	5	8	350	348
3	5	-8	8-	-9
3	7	8	82	-86
3	7	-8	330	332
3	1	9	458	437
3	1	-9	334	-353
3	3	9	19	-16
3	3	-9	44	48
3	5	9	8-	11
3	5	-9	131	-132
3	7	9	57	-62
3	7	-9	41	-39
3	1	10	65	68
3	1	-10	287	298
3	3	10	154	-160
3	3	-10	19	14
3	5	10	62	64
3	5	-10	58	-58
3	7	-10	46	-44
3	1	11	370	-369
3	1	-11	220	-235
3	3	11	8-	8
3	3	-11	276	298
3	5	11	50	-53
3	5	-11	94	94
3	1	12	56	-61
3	1	-12	14-	11
3	3	12	175	-174
3	3	-12	71	-90
3	5	-12	314	315
3	1	13	98	-93
3	1	-13	41	-53
3	3	-13	50	-75
3	1	-14	100	142
4	0	0	1001	1085
4	2	0	205	-209
4	4	0	410	388
4	6	0	142	-138
4	8	0	274	-275
4	10	0	290	283
4	2	1	728	-757
4	2	-1	264	240
4	4	1	235	215
4	4	-1	883	857
4	6	1	114	-111
4	6	-1	500	-495
4	8	1	303	311
4	8	-1	167	165
6	10	1	130	129
4	10	-1	72	-68
4	0	2	503	-513
4	0	-2	548	511
4	2	2	572	538
4	2	-2	287	-303
4	4	2	15-	-12
4	4	-2	118	114
4	6	2	294	290
4	6	-2	493	485
4	8	2	351	357
4	8	-2	19-	-16
4	10	2	239	-234
4	10	-2	79	94
4	2	3	297	277
4	2	-3	230	-203
4	4	3	412	402
4	4	-3	518	-520
4	6	3	204	-208
4	6	-3	556	554
4	8	3	36	-28
4	8	-3	35	37
4	10	-3	143	146
4	0	4	253	-233
4	0	-4	595	566
4	2	4	866	855
4	2	-4	149	-144
4	4	4	52	-50
4	4	-4	227	201
4	6	4	252	-247
4	6	-4	186	-182
4	8	4	207	216
4	8	-4	263	-259
4	10	-4	236	228
4	2	5	89	-98
4	2	-5	794	822
4	4	5	391	-394
4	4	-5	197	-176
4	6	5	252	248
4	6	-5	357	358
4	8	5	21-	30
4	8	-5	246	-239
4	0	6	107	-103
4	0	-6	404	-424
4	2	6	101	95
4	2	-6	51	39
4	4	6	186	188
4	4	-6	30	-27
4	6	6	227	231
4	6	-6	169	164
4	8	6	107	110
4	8	-6	212	209
4	2	7	415	398
4	2	-7	167	-158
4	4	7	237	-239
4	4	-7	216	-198
4	6	7	299	307
4	6	-7	209	209
4	8	7	244	-260
4	8	-7	141	140
4	0	8	661	653
4	0	-8	397	-375
4	2	8	82	-68
4	2	-8	476	470
4	4	8	80	74
4	4	-8	250	-239
4	6	8	19-	-26
4	6	-8	288	-283
4	8	-8	141	139
4	2	9	21-	-31
4	2	-9	87	90
4	4	9	199	-205
4	4	-9	363	360
4	6	9	26	28
4	6	-9	110	-111
4	8	-9	12-	10
4	0	10	91	91
4	0	-10	366	-371
4	2	10	128	-129
4	2	-10	27	-32
4	4	10	176	187
4	4	-10	10-	-6
4	6	10	180	193
4	6	-10	94	96
4	2	11	140	-134
4	2	-11	203	-231
4	4	11	300	311
4	4	-11	129	128
4	6	-11	152	-145
4	0	12	289	284
4	0	-12	331	367
4	2	12	26-	-22
4	2	-12	177	-210
4	4	-12	41	-34
4	2	-13	10-	-12
4	4	-13	212	208
4	0	-14	84	-82
5	1	0	615	-610
5	3	0	198	-190
5	5	0	353	348
5	7	0	105	-112
5	9	0	19-	-20
5	1	1	290	-279
5	1	-1	576	-570
5	3	1	359	361
5	3	-1	246	230
5	5	1	327	330
5	5	-1	221	-204
5	7	1	173	-173
5	7	-1	47	-47
5	9	1	10-	7
5	9	-1	441	447
5	1	2	8-	4
5	1	-2	381	378
5	3	2	280	272
5	3	-2	765	-768
5	5	2	896	-901
5	5	-2	55	52
5	7	2	256	265
5	7	-2	445	-451
5	9	2	131	-130
5	9	-2	81	78
5	1	3	252	-224
5	1	-3	82	89
5	3	3	76	67
5	3	-3	221	229
5	5	3	173	-162
5	5	-3	182	187
5	7	3	76	79
5	7	-3	55	-65
5	9	3	286	295
5	9	-3	195	-193
5	1	4	509	-490
5	1	-4	464	-434
5	3	4	287	277
5	3	-4	377	-362
5	5	4	51	-46
5	5	-4	355	349
5	7	4	168	175
5	7	-4	109	-109
5	9	4	55	-63
5	9	-4	10-	-11
5	1	5	538	534
5	1	-5	537	511
5	3	5	117	-105
5	3	-5	609	-589
5	5	5	259	255
5	5	-5	105	-99
5	7	5	143	149
5	7	-5	296	298
5	9	-5	119	-121
5	1	6	202	197
5	1	-6	5-	3
5	3	6	108	-107
5	3	-6	93	-84
3	5	6	184	-191
5	5	-6	369	-362
5	7	6	71	-69
5	7	-6	139	-136
5	9	-6	36	-39
5	1	7	321	301
5	1	-7	440	439
5	3	7	279	-273
5	3	-7	36	36
5	5	7	65	-62
5	5	-7	76	80
5	7	7	217	230
5	7	-7	30	-28
5	1	8	61	-59
5	1	-8	388	371
5	3	8	176	-169
5	3	-8	164	150
5	5	8	336	351
5	5	-8	228	-221
5	7	8	76	-78
5	7	-8	264	264
5	1	9	8-	-9
5	1	-9	392	-389
5	3	9	180	181
5	3	-9	71	-71
5	5	9	89	89
5	5	-9	101	-93
5	7	-9	10-	9
5	1	10	182	181
5	1	-10	70	-67
5	3	10	153	-151
5	3	-10	189	195
5	5	10	120	121
5	5	-10	387	-382
5	7	-10	21	21
5	1	11	272	-272
5	1	-11	36	-40
5	3	11	55	59
5	3	-11	214	226
5	5	-11	10-	11
5	1	12	24-	-30
5	1	-12	33	-37
5	3	-12	188	-228
5	5	-12	200	201
5	1	-13	214	-271
5	3	-13	30	-35
6	0	0	86	-61
6	2	0	184	184
6	4	0	149	-164
6	6	0	274	-276
6	8	0	55	-59
6	2	1	642	-648
6	2	-1	7-	1
6	4	1	93	100
6	4	-1	456	460
6	6	1	267	-281
6	6	-1	398	-401
6	8	1	180	189
6	8	-1	57	-56
6	0	2	823	-807
6	0	-2	323	314
6	2	2	280	275
6	2	-2	600	-575
6	4	2	253	-252
6	4	-2	247	257
6	6	2	69	73
6	6	-2	301	304
6	8	2	291	298
6	8	-2	162	-166
6	2	3	313	307
4	2	-3	320	-303
6	4	3	99	105
6	4	-3	212	-217
6	6	3	134	-140
6	6	-3	137	-134
6	8	3	128	-127
6	8	-3	113	109
6	0	4	189	-176
6	0	-4	828	876
6	2	4	99	109
6	2	-4	255	-235
6	4	4	76	-83
6	4	-4	19-	16
6	6	4	306	-315
6	6	-4	113	-109
6	8	4	43	-38
6	8	-4	197	-204
6	2	5	35	32
6	2	-5	313	299
6	4	5	604	-620
6	4	-5	175	-171
6	6	5	468	470
6	6	-5	191	194
6	8	5	161	-165
6	8	-5	286	-291
6	0	6	202	-193
6	0	-6	461	-433
6	2	6	160	-160
6	2	-6	62	98
6	4	6	114	-119
6	4	-6	148	145
6	6	6	118	123
6	6	-6	202	202
6	8	-6	46	51
6	2	7	285	287
6	2	-7	151	152
6	4	7	12-	-15
6	4	-7	601	-609
6	6	7	8-	-9
6	6	-7	249	245
6	8	-7	110	-112
6	0	8	361	366
6	0	-8	220	204

Table III. (Continued)

h	k	l	$10F_o$	$10F_c$	h	k	:	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k	l	$10F_o$	$10F_c$	h	k		$10F_o$	$10F_c$	h	k	.	$10F_o$	$10F_c$	h	k		$10F_o$	$10F_c$
6	2	8	318	-318	7	3	2	380	370	7	1	-7	658	640	8	0	2	605	-617	8	4	7	65	67	9	1	4	132	-131	10	4	2	47	44
6	2	-8	284	290	7	3	-2	35	28	7	3	7	85	-85	8	0	-2	405	-401	8	4	-7	349	-358	9	1	-4	96	-98	10	4	-2	121	133
6	4	8	67	69	7	5	2	382	-385	7	3	-7	5-	-1	8	2	2	272	264	8	6	-7	184	187	9	3	4	159	-161	10	2	3	117	121
6	4	-8	132	-127	7	5	-2	133	137	7	5	7	160	-166	8	2	-2	112	-101	8	0	8	363	362	9	3	-4	329	-323	10	2	-3	312	-308
6	6	8	96	-104	7	7	2	141	148	7	5	-7	86	75	8	4	2	30	33	8	0	-8	92	-86	9	5	4	80	83	10	4	3	76	-79
6	6	-8	185	-179	7	7	-2	202	-211	7	7	-7	43	49	8	4	-2	121	124	8	2	8	105	-109	9	5	-4	263	272	10	4	-3	125	141
6	2	9	198	-204	7	1	3	177	175	7	1	8	5-	-6	8	6	2	83	85	8	2	-8	175	158	9	1	5	332	329	10	0	4	370	378
6	2	-9	42	-50	7	1	-3	211	203	7	1	-8	84	-77	8	6	-2	176	173	8	4	-8	239	-237	9	1	-5	27	-26	10	0	-4	420	436
6	4	9	10-	7	7	3	3	323	-318	7	3	8	199	-201	8	8	-2	55	-60	8	6	-8	209	-210	9	3	5	10-	1	10	2	4	125	-132
6	4	-9	236	235	7	3	-3	295	281	7	3	-8	167	155	8	2	3	318	315	8	2	-9	194	194	9	3	-5	289	-274	10	2	-4	41	-33
6	6	-9	91	-93	7	5	3	131	-138	7	5	8	405	439	8	2	-3	109	-106	8	4	-9	19-	-22	9	5	5	47	45	10	4	-4	45	45
6	0	10	22-	20	7	5	-3	85	73	7	5	-8	37	-35	8	4	3	73	-81	8	0	-10	457	-444	9	5	-5	76	-73	10	2	5	85	90
6	0	-10	518	-500	7	7	3	124	131	7	7	-8	275	278	8	4	-3	10-	-19	8	2	-10	49	55	9	1	6	97	100	10	2	-5	121	119
6	2	10	218	-205	7	7	-3	157	-160	7	1	9	61	-59	8	6	3	259	267	8	4	-10	48	-55	9	1	-6	159	148	10	4	-5	116	122
6	2	-10	269	275	7	1	4	180	-179	7	1	-9	83	-86	8	6	-3	92	-97	8	2	-11	169	-173	9	3	6	214	-222	10	0	-6	164	162
6	4	10	8-	-6	7	1	-4	221	214	7	3	9	46	51	8	0	4	93	94	9	1	0	234	-248	9	3	-6	247	-243	10	2	-6	146	-146
6	4	-10	86	87	7	3	4	280	281	7	3	-9	202	-196	8	0	-4	766	775	9	3	0	8-	-7	9	5	-6	83	89	10	4	-6	132	134
6	6	-10	113	110	7	3	-4	387	-380	7	5	-9	19-	19	8	2	4	201	197	9	5	0	136	-142	9	1	7	68	-69	10	2	-7	10-	-4
6	2	11	12-	-17	7	5	4	68	68	7	1	10	108	111	8	2	-4	384	-379	9	1	1	296	296	9	1	-7	332	320	10	4	-7	319	-325
6	2	-11	159	-172	7	5	-4	668	682	7	1	-10	46	47	8	4	4	62	-67	9	1	-1	587	-576	9	3	-7	26	-24	10	0	-8	257	244
6	4	-11	54	49	7	7	4	180	193	7	3	-10	237	240	8	4	-4	75	-77	9	3	1	108	107	9	5	-7	36	34	10	2	-8	33	34
6	0	-12	291	298	7	7	-4	91	-90	7	5	-10	232	-231	8	6	4	126	-130	9	3	-1	10-	9	9	1	-8	187	-181	11	1	0	123	-126
6	2	-12	58	58	7	1	5	455	436	7	1	-11	116	-116	8	6	-4	108	-103	9	5	1	48	40	9	3	-8	48	41	11	3	0	261	270
6	4	-12	38	-34	7	1	-5	106	-102	7	3	-11	296	287	8	2	5	34	28	9	5	-1	57	-53	9	5	-8	36	37	11	1	1	171	175
6	2	-13	31	-34	7	3	5	176	-170	7	1	-12	76	-78	8	2	-5	176	160	9	7	-1	30	-31	9	1	-9	55	55	11	1	-1	169	-161
7	1	0	103	-97	7	3	-5	296	-287	7	3	-12	36	31	8	4	5	273	-286	9	1	2	144	-143	9	3	-9	193	-186	11	3	1	70	71
7	3	0	306	295	7	5	5	98	106	8	0	0	143	138	8	4	-5	97	82	9	1	-2	12-	-14	9	1	-10	39	36	11	3	-1	31	-36
7	5	0	53	59	7	5	-5	40	-35	8	2	0	209	205	8	6	5	205	220	9	3	2	277	276	10	0	0	57	-54	11	1	2	100	105
7	7	0	324	332	7	7	5	55	53	8	4	0	195	-208	8	6	-5	181	180	9	3	-2	36	-29	10	2	0	331	326	11	1	-2	136	134
7	1	1	223	-208	7	7	-5	246	241	8	6	0	204	-206	8	0	6	212	220	9	5	2	436	-460	10	4	0	164	-173	11	3	-2	109	115
7	1	-1	662	-664	7	1	6	272	271	8	8	0	98	100	8	0	-6	179	-171	9	5	-2	150	-158	10	2	1	8-	-6	11	1	3	133	138
7	3	1	366	359	7	1	-6	207	195	8	2	1	96	-90	8	2	6	212	-219	9	7	-2	161	-174	10	2	-1	52	-45	11	1	-3	151	-154
7	3	-1	30	27	7	3	6	102	-105	8	2	-1	207	-210	8	2	-6	323	-317	9	1	3	54	52	10	4	1	220	-230	11	3	-3	225	223
7	5	1	70	67	7	3	-6	179	183	8	4	1	55	-63	8	4	6	139	151	9	1	-3	133	-130	10	4	-1	233	245	11	1	-4	46	-48
7	5	-1	89	-87	7	5	6	12-	-15	8	4	-1	655	669	8	4	-6	159	156	9	3	3	265	-270	10	0	2	466	-468	11	3	-4	96	-89
7	7	1	228	-237	7	5	-6	51	-54	8	6	1	19-	-20	8	6	-6	136	130	9	3	-3	362	357	10	0	-2	154	-157	11	1	-5	201	-199
7	7	-1	33	-42	7	7	-6	99	-102	8	6	-1	266	-276	8	2	7	150	156	9	5	3	22-	-21	10	2	2	175	169	11	3	-5	64	62
7	1	2	238	235	7	1	7	26	-20	8	8	-1	130	138	8	2	-7	108	103	9	5	-3	8-	-9	10	2	-2	10-	-7	11	1	-6	211	205
7	1	-2	394	384																														

Table IV. Atomic peak heights (e. Å^{-3}), curvatures (e. Å^{-5}) and e.s.d.'s.

		ρ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	$-A_{hk}$	A_{hl}	A_{kl}
Cl	obs.	42.8	478	447	430	—5	56	—16
	calc.	43.0	481	449	434	—5	57	—17
S	obs.	41.8	469	466	427	0	85	—12
	calc.	42.1	471	464	432	0	84	—12
O_w	obs.	15.4	158	149	143	0	20	—4
	calc.	15.5	158	150	146	1	19	—4
N(1)	obs.	13.3	126	127	122	7	14	—3
	calc.	13.3	127	128	123	7	14	—3
N(2)	obs.	13.9	137	130	137	10	15	—4
	calc.	13.9	138	130	137	10	15	—4
C	obs.	12.2	120	114	130	0	5	—2
	calc.	12.3	121	115	133	0	6	—3
e.s.d.		0.1	1	1	2	1	1	1

		ρ			ρ			ρ
H(1.1)	obs.	1.3	H(2.2)	obs.	0.5	H(5)	obs.	0.6
	calc.	1.4		calc.	0.5		calc.	0.9
H(2.1)	obs.	1.4	H(2.3)	obs.	0.8	H(6)	obs.	1.0
	calc.	1.6		calc.	1.1		calc.	1.3

Table V. Main interatomic bond distances and angles.

C-S	1.645(3) Å	S-C-N(1)	124.4(1)°
C-N(1)	1.363(5)	C-N(1)-N(2)	117.8(2)
N(1)-N(2)	1.418(6)	N(1)-C-N(1^i)	111.1(2)
N(1)-H(1.1)	0.97	C-N(1)-H(1.1)	119.7
N(2)-H(2.1)	0.93	N(2)-N(1)-H(1.1)	113.1
N(2)-H(2.2)	0.90	N(1)-N(2)-H(2.1)	108.4
N(2)-H(2.3)	0.96	N(1)-N(2)-H(2.2)	110.9
O_w-H(5)	0.91	N(1)-N(2)-H(2.3)	114.0
O_w-H(6)	1.03	H(2.1)-N(2)-H(2.2)	112.8
		H(2.1)-N(2)-H(2.3)	94.5
		H(2.2)-N(2)-H(2.3)	115.0
		H(5)-O_w-H(6)	115.9

Asymmetric unit transformation: i 1—*x*, *y*, ½—*x*

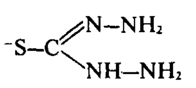
Table VI. Hydrogen bonds.

$N(2)\ldots O_w^{ii}$	2.789(4) Å	$O_w\ldots N(2)\ldots Cl^{iii}$	105.6(1)°
$H(2.1)\ldots O_w^{ii}$	1.895	$O_w\ldots N(2)\ldots O_w^{ii}$	90.1(1)
$N(2)\ldots Cl^{iii}$	3.199(6)	$N((1)\text{-}N(2)\ldots Cl^{iii}$	104.7(2)
$H(2.2)\ldots Cl^{iii}$	2.306	$N(1)\text{-}N(2)\ldots O_w^{ii}$	102.3(1)
$N(2)\ldots O_w$	2.882(4)	$N(1)\text{-}N(2)\ldots O_w$	127.3(1)
$H(2.3)\ldots O_w$	1.969	$O_w^{ii}\ldots N(2)\ldots Cl^{iii}$	129.7(1)
$N(1)\ldots Cl^{iv}$	3.175(4)	$N(2)\text{-}N(1)\ldots Cl^{iv}$	111.0(2)
$H(1.1)\ldots Cl^{iv}$	2.207	$C\text{-}N(1)\ldots Cl^{iv}$	121.3(2)
$O_w\ldots Cl$	3.250(6)	$Cl\ldots O_w\ldots N(2)$	121.0(1)
$H(5)\ldots Cl$	2.382	$N(2)\ldots O_w\ldots N(2^{ii})$	89.9(1)
$O_w\ldots Cl^v$	3.191(9)	$Cl\ldots O_w\ldots Cl^v$	88.6(1)
$H(6)\ldots Cl^v$	2.270	$N(2^{ii})\ldots O_w\ldots Cl^v$	81.5(1)
		$Cl\ldots O_w\ldots N(2^{ii})$	142.2(1)
		$Cl^v\ldots O_w\ldots N(2)$	135.9(1)
		$N(2)\text{-}H(2.1)\ldots O_w^{ii}$	161.8
		$N(2)\text{-}H(2.2)\ldots Cl^{iii}$	170.9
		$N(2)\text{-}H(2.3)\ldots O_w$	158.4
		$N(1)\text{-}H(1.1)\ldots Cl^{iv}$	176.8
		$O_w\text{-}H(5)\ldots Cl$	159.7
		$O_w\text{-}H(6)\ldots Cl^v$	147.7

Asymmetric unit transformations:

ii	$1/2-x$	$1/2-y$	$1-z$
iii	$1/2-x$	$1/2+y$	$1/2-z$
iv	x	$1+y$	z
v	$1/2-x$	$-1/2-y$	$1-z$

$C{-}S = 1.724(10)$ Å and $C{-}N = 1.315(11)$, $1.335(9)$ Å. These distances clearly indicate that when passing from neutral to cation species the double bond character is transferred from C–N to C–S. This is in accordance with findings in solution[2] where in acidic media there are mono- and diprotonated cations in which very likely the electron cloud is attracted from S toward the S–C bond; on the other hand in alkaline media the single bond character of C–S with electrons refluxing toward S is so pronounced that deprotonation equilibria due to the thio-enolic form



$$^{-}S{-}C\begin{matrix}\nearrow N{-}NH_2\\ \searrow NH{-}NH_2\end{matrix}$$

are involved.

The average nitrogen-hydrogen distance, $N{-}H_{av} = 0.94 \pm 0.04$ Å agrees with values generally found in x-ray structure determinations.[6]

The anion-cation interactions (Figure 3) correspond to hydrogen bonds $N(1)\ldots Cl = 3.175(4)$ and $N(2)\ldots Cl = 3.199(6)$ Å. Further hydrogen bonds $N(2)\ldots O_w = 2.882(4)$, $2.789(4)$ Å complete the tetrahedral environment of the planar ends $-\overset{+}{N}H_3$. Also the environment of the water molecule (Figure 4) is very roughly speaking tetrahedral with a pair of hydrogen bonds of type $O_w\ldots Cl = 3.191(9)$, $3.250(6)$ Å and a pair of type $N(2)\ldots O_w$.

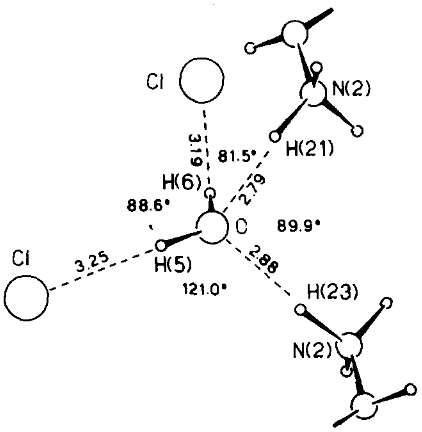


Figure 4. Environment of the water molecule, O_w.

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(6) Y. Tomiie, *Acta Cryst.*, *11*, 875 (1958).