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The Crystal Structure of Thiosemicarbazide

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The crystal structure of thiosemicarbazide has been determined by three-dimensional X-ray diffraction methods. 826 significant reflexions were measured on a diffractometer and refinement of coordinates and anisotropic temperature factor parameters by the methods of least-squares was carried out to an R-value of 6.0 %. The triclinic cell ($P\bar{1}$) of dimensions $a=6.008$ Å, $b=4.925$ Å, $c=7.311$ Å, $\alpha=76.99°$, $\beta=102.79°$, $\gamma=96.27°$ contains two molecules. The molecule is planar with the exception of the hydrogen atoms at the terminal hydrazine nitrogen atom. This nitrogen atom is as far away from sulphur as possible. The bond lengths are: C–S=1.701 Å, C–N=1.320, 1.325 Å, N–N=1.412 Å in close agreement with the values found in most thiosemicarbazide complexes. Bond lengths corrected for vibrational effects are given in the paper.

The structures of several thiosemicarbazide complexes have been studied in this laboratory [1-4] and at the University of Parma. [5-7] It was desirable to know the structure of the free molecule for comparison of bond lengths and angles.

The crystals used in the X-ray analysis were obtained by the recrystallisation from water of a commercial product. The crystal used for intensity measurements was $0.25\times0.25\times0.45$ mm^3. Weissenberg, Rimsky-retigraph-, and precession exposures were made of differently oriented crystals. A triclinic unit cell with dimensions: $a=6.008$ Å, $b=4.925$ Å, $c=7.311$ Å, $\alpha=76.99°$, $\beta=102.79°$, $\gamma=96.27°$, was chosen, (if the a-axis was reversed a Delaunay cell with all angles acute could be obtained). The crystal is elongated in the $[10\bar{1}]$ direction, $d(10\bar{1})=8.33$ Å. The cell dimensions were refined by the method of least squares from measurements of 26 lines on a Guinier film taken with Cu$K\alpha_1$ radiation ($\lambda=1.5404$ Å) with NaCl ($a=5.6389$ Å) as an internal standard. Intensities were obtained by means of an automatic diffractometer of the Arndt-Phillips design,[8] using Mo$K\alpha$ radiation and balanced filter technique. No correction for absorption was applied ($\mu r_{\max}=0.25$).

STRUCTURE DETERMINATION

The structure was solved from the Patterson projection $P(u,w)$ and confirmed from the three-dimensional Patterson function. Space group $P\bar{1}$ was assumed and no indication has been found of lower symmetry.

Refinement was carried out by the method of least squares using the block diagonal approximation.[9,10] At $R=7.5$ % a difference Fourier synthesis was calculated, which showed 5 peaks of height 0.5 e/Å^3 at positions where hydrogen atoms could be expected; all other peaks were less than 0.3 e/Å^3. After inclusion of the hydrogen atoms further refinement reduced R to 6.0 %. The weights used at the end of the refinement were: $w = 1/\mu(F)^2$ where

$$\mu(F) = \sqrt{F^2 + \sigma F^2_{\text{count}} + K \cdot F^2} - |F|$$

$\sigma F^2_{\text{count}}$ is the standard deviation obtained from the counting statistics; $K \cdot F^2$ is a term which should account for other errors, K is adjusted so that $w\Delta^2$ is approximately independent of the size of F ($K=0.037$). Reflexions for which $F^2 < 2\sigma F^2_{\text{count}}$ were left out of the refinement, leaving 826 significant reflexions. Full matrix refinement[11] was attempted in the end in the hope of better determination of the hydrogen atom parameters but no improvement was found. The temperature factor parameters of the hydrogen atoms tended to decrease, some to negative values so they had to be fixed at reasonable values. Their positional parameters stayed close to the expected values.

CRYSTAL DATA

Thiosemicarbazide: CH_5N_3S
Crystal system: Triclinic
Unit cell parameters with estimated standard deviations:

a = 6.008 Å (0.005); b = 4.925 Å (0.005); c = 7.311 Å (0.006)
α = 76.99° (0.05°); β = 102.79°(0.04°); γ = 96.27° (0.04°)
V = 206 Å^3; d_{obs} = 1.48 g/cm^3; d_{calc} = 1.47 g/cm^3; $Z = 2$; μ_{Mo} = 5.7 cm^{-1}

No piezoelectric effect could be detected.
Space group: $P\bar{1}$ (from the structure analysis).

Final coordinates and anisotropic temperature factor parameters are given in Table 1, bond lengths and angles in Table 2, and a list of observed and calculated structure factors in Table 3.

DISCUSSION

The thiosemicarbazide molecule is nearly planar. The carbon atom is 0.02 Å from the plane of S, N_2, and N_3 whereas N_1 is 0.03 Å on the other side of this plane. The hydrogen atoms at N_1 are placed nearly symmetrically on either side of this plane whereas the other three hydrogen atoms are in the plane. Carbon and its two neighbouring nitrogen atoms are thus very well described as trigonally hybridized; the terminal nitrogen atom of the hydrazine group is tetrahedrally hybridized.

Table 1. Final atomic parameters.

a. Coordinates; standard deviations × 10^4 in parentheses.

	x	σx	y	σy	z	σz
S	0.8210	(2)	−0.0012	(3)	0.1951	(2)
C	0.6633	(7)	0.1840	(8)	0.2848	(5)
N_1	0.3283	(6)	0.4249	(9)	0.2473	(6)
N_2	0.4618	(6)	0.2634	(8)	0.1812	(5)
N_3	0.7392	(7)	0.2607	(8)	0.4505	(5)
H_{11}	0.2988	(119)	0.5876	(138)	0.1458	(104)
H_{12}	0.2012	(126)	0.3225	(137)	0.2501	(100)
H_{21}	0.3963	(121)	0.1745	(135)	0.0734	(102)
H_{31}	0.8913	(122)	0.2095	(139)	0.5345	(102)
H_{32}	0.6506	(113)	0.3666	(128)	0.4788	(95)

b. Anisotropic temperature factor parameters, $u_{ij} \times 10^5$, with standard deviations in parentheses.

	u_{11}	σu_{11}	u_{22}	σu_{22}	u_{33}	σu_{33}	u_{12}	σu_{12}	u_{13}	σu_{13}	u_{23}	σu_{23}
S	3372	(61)	7054	(75)	3684	(62)	1538	(51)	−542	(43)	−2417	(54)
C	2842	(195)	4139	(183)	2860	(194)	127	(161)	49	(154)	− 663	(161)
N_1	3360	(188)	6275	(225)	3754	(199)	960	(183)	346	(166)	−1266	(180)
N_2	2927	(178)	6458	(213)	3077	(179)	969	(165)	−212	(144)	−1540	(168)
N_3	4028	(217)	6534	(218)	3344	(194)	1774	(184)	−665	(163)	−2020	(178)

The temperature factors for the hydrogen atoms were fixed at $B = 5.0$.

The bond lengths suggest that the double bond is delocalised over the CSNN system in such a way as to give the two C—N bonds the same bond order. All bond lengths agree very closely with the values found in most of the complexes as seen from Table 4. The angles show a little more variation because of the complex formation. The thiosemicarbazidato nickel[7] has significantly different distances from those of the other compounds as could be expected because of the loss of a hydrogen ion. The silver complex[6] and the free molecule have the terminal hydrazine nitrogen placed as far from sulphur as possible in contrast to the nickel complexes where thiosemicarbazide acts as a bidentate ligand and therefore has these two atoms next to one another; this fact seems not to influence bond lengths and angles to any significant degree.

In Table 2 are given both the directly calculated bond lengths and the ones corrected for thermal motion according to the following model: most of the thermal motion can be described as translational movement of the molecule as a whole, especially perpendicular to the plane of the molecule. The rest seems to be reasonably described as rigid body vibration of S, C, N_2, and N_3[13] whereas the motion of N_1 is best described as a riding motion on N_2.[14] In any case the corrections are small and not very dependent on the model.

Table 2. Distances and angles.

Uncorrected and corrected for thermal motion, standard deviations × 10^3 in parentheses.

Bond	uncorr.	corr.	e.s.d.	Bond	uncorr. dist.	e.s.d.
$S-C$	1.701	1.713	(5)	N_1-H_{11}	0.964	(62)
$C-N_2$	1.325	1.334	(5)	N_1-H_{12}	0.869	(70)
$C-N_3$	1.320	1.331	(6)	N_2-H_{21}	0.974	(74)
N_2-N_1	1.412	1.415	(6)	N_3-H_{31}	1.004	(66)
				N_3-H_{32}	0.869	(76)

Angles in degrees with standard deviations.

$S-C-N_2$	118.84	(0.33)
$S-C-N_3$	122.11	(0.31)
N_2-C-N_3	118.98	(0.42)
$C-N_2-N_1$	120.81	(0.37)
$C-N_2-H_{21}$	117.14	(4.30)
$C-N_3-H_{31}$	122.73	(4.79)
$C-N_3-H_{32}$	114.86	(4.13)
$N_2-N_1-H_{11}$	104.80	(5.06)
$N_2-N_1-H_{12}$	103.05	(5.38)
$H_{11}-N_1-H_{12}$	108.36	(5.71)
$H_{31}-N_3-H_{32}$	122.40	(6.10)

Some intermolecular distances. The symmetry operation applied to the second atom is given in parentheses.

N_1-N_3	3.085	$(1-x, 1-y, 1-z)$
$S-N_2$	3.398	$(2-x, -y, 1-z)$
$S-N_2$	3.343	$(1-x, -y, -z)$
$S-N_1$	3.505	$(1+x, y, z)$
$S-N_1$	3.802	$(1-x, 1-y, -z)$
$S-N_1$	3.884	$(x, -1+y, z)$
$S-N_3$	3.729	$(x, -1+y, z)$
$S-S$	3.931	$(2-x, -y, -z)$

The bond lengths given for thiourea in [12] are corrected for vibration effects so the corrected bond lengths should be used for comparison with these; in all other cases uncorrected distances are given.

Two neighbouring molecules are nearly coplanar, the biggest deviations from the common plane of the heavier atoms being 0.03 Å. Fig. 1 shows a projection of part of the structure on to this plane. The intermolecular N_1-N_3 distance of 3.08 Å is too long for a strong hydrogen bond in agreement with the fact that the hydrogen atom of N_3 and the lone pair of N_1 are not aligned along the N_1-N_3 direction. On the other hand some interaction is likely between the other hydrogen atoms and the sulphur atoms of other molecules. Two short N—H—S bonds (3.34 and 3.39 Å) are found in the plane of Fig. 1

Table 3. Observed and calculated structure factors × 10. A < after a reflexion means that it is not significant and has been left out of the refinements.

h	k	l	Fobs	Fcal
0	0	1	10	-4
0	0	2	328	-334
0	0	3	265	271
0	0	4	126	123
0	0	5	108	-115
0	0	6	26	28
0	0	7	14	21
0	0	8	59	-63
0	0	9	7	6 <
1	0	-9	45	50
1	0	-8	8	-3 <
1	0	-7	88	-97
1	0	-6	9	5 <
1	0	-5	23	23
1	0	-4	110	-114
1	0	-3	15	-15
1	0	-2	48	-50
1	0	-1	198	-198
1	0	0	131	128
1	0	1	182	179
1	0	2	67	-62
1	0	3	3	-9 <
1	0	4	143	144
1	0	5	40	36
1	0	6	29	-27
1	0	7	44	46
1	0	8	22	23
1	0	9	23	-25
2	0	-9	11	-4 <
2	0	-8	35	39
2	0	-7	26	21
2	0	-6	66	-65
2	0	-5	4	11 <
2	0	-4	60	60
2	0	-3	149	-146
2	0	-2	108	-112
2	0	-1	129	132
2	0	0	251	-253
2	0	1	272	-269
2	0	2	202	208
2	0	3	22	22
2	0	4	191	-196
2	0	5	44	42
2	0	6	96	100
2	0	7	34	-40
2	0	8	14	-2 <
2	0	9	34	35
3	0	-9	11	-11 <
3	0	-8	40	-43
3	0	-7	80	82
3	0	-6	62	68
3	0	-5	108	-112
3	0	-4	37	36
3	0	-3	176	176
3	0	-2	76	-79
3	0	-1	15	-12
3	0	0	73	78
3	0	1	172	-163
3	0	2	43	-43
3	0	3	123	127
3	0	4	102	-107
3	0	5	127	-128
3	0	6	67	74
3	0	7	19	16
3	0	8	59	-62
4	0	-9	12	0 <
4	0	-8	28	-32
4	0	-7	20	-8
4	0	-6	63	67
4	0	-5	14	-15
4	0	-4	84	-88
4	0	-3	82	85
4	0	-2	119	121
4	0	-1	57	-58
4	0	0	10	-5 <
4	0	1	109	115
4	0	2	13	-10
4	0	3	38	-37
4	0	4	55	58
4	0	5	19	1
4	0	6	54	-57
4	0	7	15	3 <
5	0	-9	14	-21
5	0	-8	17	6
5	0	-7	10	5 <
5	0	-6	45	-46
5	0	-5	0	7 <
5	0	-4	34	38
5	0	-3	82	-83
5	0	-2	33	-28
5	0	-1	99	100
5	0	0	28	-28
5	0	1	36	-40
5	0	2	87	87
5	0	3	4	-2 <
5	0	4	24	-29
5	0	5	77	81
5	0	6	9	10 <
6	0	-7	16	22
6	0	-6	12	-16 <
6	0	-5	36	-37
6	0	-4	57	60
6	0	-3	11	3 <
6	0	-2	122	-124
6	0	-1	19	19
6	0	0	84	86
6	0	1	79	-83
6	0	2	50	-53
6	0	3	55	61
6	0	4	4	-8 <
6	0	5	14	-21
7	0	-7	6	-11 <
7	0	-6	0	8 <
7	0	-5	9	15
7	0	-4	11	0 <
7	0	-3	16	11
7	0	-2	8	4 <
7	0	-1	26	-28
7	0	0	0	6 <
7	0	1	26	25
7	0	2	30	-34
-8	1	-1	10	-15 <
-8	1	0	40	38
-8	1	1	0	-9 <
-7	1	-1	60	-59
-7	1	0	22	22
-7	1	1	63	64
-7	1	2	32	-33
-7	1	3	0	-1 <
-7	1	4	54	53
-7	1	5	17	-15 <
-7	1	6	21	-23
-7	1	7	23	21
-6	1	-5	14	17 <
-6	1	-4	7	0 <
-6	1	-3	68	-68
-6	1	-2	11	-5 <
-6	1	-1	47	51
-6	1	0	44	-40
-6	1	1	45	-43
-6	1	2	32	36
-6	1	3	10	13 <
-6	1	4	0	-4 <
-6	1	5	24	29
-6	1	6	6	-2 <
-6	1	7	14	-13 <
-5	1	-5	32	-32
-5	1	-4	56	56
-5	1	-3	5	6 <
-5	1	-2	121	-129
-5	1	-1	51	50
-5	1	0	101	103
-5	1	1	164	-168
-5	1	2	79	-83
-5	1	3	122	124
-5	1	4	31	-37
-5	1	5	70	-77
-5	1	6	46	49
-5	1	7	19	6
-5	1	8	24	-28
-5	1	9	22	25
-4	1	-7	18	-27
-4	1	-6	69	72
-4	1	-5	20	18
-4	1	-4	40	-42
-4	1	-3	82	81
-4	1	-2	45	40
-4	1	-1	68	-68
-4	1	0	87	83
-4	1	1	55	58
-4	1	2	106	-109
-4	1	3	0	-13 <
-4	1	4	39	39
-4	1	5	56	-54
-4	1	6	28	-32
-4	1	7	14	19
-4	1	8	26	-26
-4	1	9	24	-20
-3	1	-7	22	-23
-3	1	-6	47	-45
-3	1	-5	37	34
-3	1	-4	19	17
-3	1	-3	59	-55
-3	1	-2	69	75
-3	1	-1	89	85
-3	1	0	99	-101
-3	1	1	70	74
-3	1	2	258	254
-3	1	3	81	-78
-3	1	4	119	-117
-3	1	5	128	134
-3	1	6	41	40
-3	1	7	76	-83
-3	1	8	0	-1 <
-3	1	9	18	17
-2	1	-8	16	-19 <
-2	1	-7	73	76
-2	1	-6	54	-48
-2	1	-5	154	-156
-2	1	-4	84	82
-2	1	-3	68	68
-2	1	-2	233	-229
-2	1	-1	27	-29
-2	1	0	99	96
-2	1	1	150	-150
-2	1	2	147	136
-2	1	3	163	160
-2	1	4	139	-137
-2	1	5	14	14 <
-2	1	6	158	163
-2	1	7	20	-19
-2	1	8	48	-49
-2	1	9	46	50
-1	1	-8	21	-17
-1	1	-7	36	34
-1	1	-6	63	64
-1	1	-5	83	-84
-1	1	-4	61	-57
-1	1	-3	155	158
-1	1	-2	94	-84
-1	1	-1	315	-318
-1	1	0	45	44
-1	1	1	9	-7
-1	1	2	280	-280
-1	1	3	51	-45
-1	1	4	91	93
-1	1	5	86	-82
-1	1	6	56	-53
-1	1	7	70	71
-1	1	8	25	26
-1	1	9	25	-22
0	1	-8	35	35
0	1	-7	0	-3 <
0	1	-6	16	-21
0	1	-5	120	112
0	1	-4	61	62
0	1	-3	138	-128
0	1	-2	104	101
0	1	-1	333	334
0	1	1	197	-196
0	1	2	119	109
0	1	3	97	-91
0	1	4	72	-65
0	1	5	50	51
0	1	6	95	-101
0	1	7	70	-74
0	1	8	74	76
0	1	9	11	-1 <
1	1	-8	25	-22
1	1	-7	36	28
1	1	-6	45	-44
1	1	-5	0	-4 <
1	1	-4	161	154
1	1	-3	98	-93
1	1	-2	164	-159
1	1	0	249	246
1	1	1	342	-356
1	1	2	165	160
1	1	3	285	280
1	1	4	110	-110
1	1	5	40	-34
1	1	6	83	82
1	1	7	58	-56
1	1	8	40	-39
1	1	9	30	34
2	1	-8	40	-41
2	1	-7	32	-29
2	1	-6	32	32
2	1	-5	34	-34
2	1	-4	64	-60
2	1	-3	0	1 <
2	1	-2	67	-65
2	1	-1	58	-59
2	1	0	78	75
2	1	1	59	61
2	1	2	54	-53
2	1	3	49	49
2	1	4	102	98
2	1	5	6	-5 <
2	1	6	0	10 <
2	1	7	51	55
2	1	8	10	-11 <
2	1	9	17	-17 <
3	1	-8	31	29
3	1	-7	14	-16 <
3	1	-6	36	-30
3	1	-5	47	47
3	1	-4	18	-13
3	1	-3	96	-96
3	1	-2	66	63
3	1	-1	37	-36
3	1	0	251	-241
3	1	1	84	79
3	1	2	128	122
3	1	3	197	-195
3	1	4	54	-55
3	1	5	141	143
3	1	6	22	-20
3	1	7	49	-48
4	1	-8	20	20
4	1	-7	58	55
4	1	-6	44	-43
4	1	-5	36	-33
4	1	-4	100	101
4	1	-3	11	13 <
4	1	-2	55	-52
4	1	-1	54	52
4	1	0	34	-29
4	1	1	79	-75
4	1	2	77	74
4	1	3	9	-8 <
4	1	4	134	-132
4	1	5	16	13 <
4	1	6	55	50
4	1	7	56	-54
5	1	-8	13	-6 <
5	1	-7	10	18 <
5	1	-6	0	9 <
5	1	-5	35	-37
5	1	-4	4	-2 <
5	1	-3	70	68
5	1	-2	0	8 <
5	1	-1	38	-41
5	1	0	47	57
5	1	1	37	43
5	1	2	40	-46
5	1	3	28	23
5	1	4	40	50
5	1	5	41	-47
6	1	-6	0	-11 <
6	1	-5	29	32
6	1	-4	27	-26
6	1	-3	48	-54
6	1	-2	45	52
6	1	-1	21	25
6	1	0	48	-58
6	1	1	19	28
6	1	2	26	38
6	1	3	23	-34
6	1	4	32	37
6	1	5	33	41
7	1	-5	19	17
7	1	-4	12	16 <
7	1	-3	54	-50
7	1	-2	11	-19
7	1	-1	57	54
7	1	0	13	-17 <
7	1	1	59	-58
7	1	2	24	23
-8	2	0	19	-24
-8	2	1	21	22
-7	2	-2	46	-44
-7	2	-1	48	49
-7	2	0	31	25
-7	2	1	42	-43
-7	2	2	33	30
-7	2	3	23	15
-7	2	4	57	-57
-7	2	5	0	11 <
-7	2	6	32	26
-7	2	7	33	-36
-6	2	-4	18	8 <
-6	2	-3	54	52
-6	2	-2	37	-36
-6	2	-1	23	-21
-6	2	0	82	79
-6	2	1	0	1 <
-6	2	2	34	-34
-6	2	3	71	70
-6	2	4	27	27
-6	2	5	52	-51
-6	2	6	6	13 <
-6	2	7	39	37
-6	2	8	0	-17 <
-5	2	-5	21	24
-5	2	-4	54	-52
-5	2	-3	58	-57
-5	2	-2	62	65
-5	2	-1	9	3 <
-5	2	0	109	-107
-5	2	1	25	16
-5	2	2	67	66
-5	2	3	30	-32
-5	2	4	26	16
-5	2	5	38	41
-5	2	6	25	-28
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2	2	-6	19	-18
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2	5	-1	11	-9	<
2	5	0	11	11	<
2	5	1	0	0	<
2	5	2	25	-23	
2	5	3	21	15	
2	5	4	35	33	
2	5	5	10	-9	<
3	5	-1	11	6	<
3	5	0	14	-8	
3	5	1	0	2	<
3	5	2	6	-3	<
3	5	3	41	-32	
3	5	4	10	8	<
3	5	5	41	33	
4	5	-1	16	13	
4	5	0	11	14	<
4	5	1	18	-13	
4	5	2	11	1	<
4	5	3	0	0	<
-4	6	-1	4	6	<
-4	6	0	11	-15	
-4	6	1	27	-18	
-4	6	2	24	21	
-4	6	3	0	-3	<
-4	6	4	46	-39	
-4	6	5	14	8	
-4	6	6	0	17	
-3	6	-1	0	3	<
-3	6	0	21	16	
-3	6	1	12	-9	
-3	6	2	14	-16	
-3	6	3	22	22	
-3	6	4	9	7	<
-3	6	5	35	-32	
-2	6	-1	9	11	<
-2	6	0	0	-2	<
-2	6	1	6	9	<
-2	6	2	1	0	<
-2	6	3	2	-5	<
-2	6	4	32	31	
-2	6	5	16	14	
-2	6	6	38	-33	
-1	6	-2	10	-10	<
-1	6	-1	29	22	
-1	6	0	9	-4	<
-1	6	1	18	-21	
-1	6	2	7	15	
-1	6	3	0	4	<
-1	6	4	19	-14	
-1	6	5	32	26	
-1	6	6	19	14	
0	6	-2	13	-12	
0	6	-1	12	-6	
0	6	0	0	10	<
0	6	1	6	-5	<
0	6	2	6	-14	
0	6	3	3	1	<
0	6	4	10	-8	
1	6	-1	16	-14	
1	6	0	15	-11	
1	6	1	21	27	
1	6	2	8	7	<
1	6	3	29	-31	
1	6	4	7	0	<
2	6	-1	11	2	<
2	6	0	14	-14	
2	6	1	0	4	<
2	6	2	30	26	
2	6	3	16	-5	
2	6	4	20	-16	

Table 4. Comparison of bond lengths in different molecules. Thio is used as an abbreviation for thiosemicarbazide. The numbers in parentheses are the standard deviations in Å × 10^{-3}.

Compound	S—C		C—N_2		C—N_3		N_1—N_2		Ref
α-NiThio$_2$SO$_4$,3H$_2$O	1.75	(30)	1.33	(50)	1.29	(50)	1.44	(40)	1
β-NiThio$_2$SO$_4$ *cis*	1.727	(3)	1.331	(4)	1.323	(4)	1.426	(4)	2
trans	1.716	(3)	1.321	(5)	1.318	(5)	1.430	(4)	
NiThio$_2$(H$_2$O)$_2$,2NO$_3$	1.688	(3)	1.338	(5)	1.330	(5)	1.416	(5)	3
NiThio$_3$,2NO$_3$,H$_2$O	1.712	(12)	1.317	(18)	1.336	(16)	1.430	(14)	4
	1.705	(14)	1.292	(20)	1.344	(17)	1.433	(15)	
	1.721	(11)	1.326	(18)	1.339	(15)	1.428	(14)	
NiThio$_3$,2NO$_3$	1.710	(9)	1.302	(10)	1.311	(12)	1.401	(10)	4
	1.711	(8)	1.328	(11)	1.308	(11)	1.405	(9)	
	1.667	(7)	1.335	(9)	1.328	(11)	1.427	(10)	
ZnThioCl$_2$	1.73	(20)	1.28	(30)	1.29	(30)	1.44	(30)	5
AgThioCl	1.70	(40)	1.28	(40)	1.35	(40)	1.40	(40)	6
	1.74	(30)	1.37	(50)	1.29	(40)	1.38	(60)	
Ni(CH$_4$N$_3$S)$_2$	1.746	(13)	1.247	(15)	1.436	(17)	1.537	(17)	7
Thiourea	1.713	(12)	1.329	(12)	1.329	(12)			12

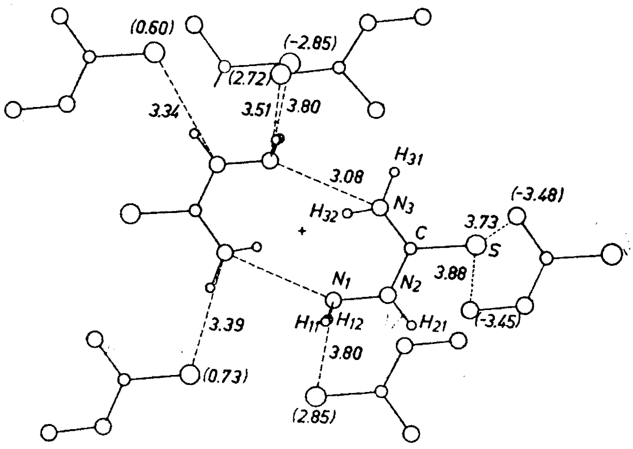

Fig. 1. Projection of part of the structure on to the best plane through two molecules. Numbers in parentheses are the distances of the atoms from this plane. The other numbers are intermolecular distances.

involving the hydrogen atom at N_2 and one of those at N_3. The hydrogen atoms at N_1 also point towards two other sulphur atoms at 3.51 Å and 3.80 Å. The hydrogen bonds are probably mainly of electrostatic character, the hybridization pattern involving partial positive charges at N_2 and N_3 and some negative charge at the sulphur atom. No other intermolecular distances are shorter than the normal van der Waals distances.

After this work was completed a short note [15] appeared in which dimensions of the thiosemicarbazide molecule are given. Some differences between the two sets of results are of the order of three to four estimated standard deviations. A closer comparison is not possible on the basis of the material published in Ref. 15.

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