The Crystal and Molecular Structure of Thiuret Hydrochloride Hemihydrate

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The crystal and molecular structure of the unsaturated fivemembered cyclic disulphide, thiuret hydrochloride hemihydrate, has been solved by systematic application of Sayre's equation, and refined by least squares methods using anisotropic temperature parameters. The refinement comprises the h0l, h1l, h2l, h3l, and hk0 reflections, and the final coordinates of the atoms in the thiuret ion have been corrected for the rigid-body libration of the ion.

The lengths of the cyclic C-N bonds in the thiuret ion are 1.342 ± 0.010 Å and 1.350 ± 0.009 Å, and the lengths of the exocyclic C-N bonds are 1.315 ± 0.009 Å and 1.303 ± 0.010 Å. The C-S bond lengths are 1.767 and 1.762 ± 0.007 Å, and the S-S

bond length is 2.071 ± 0.004 Å.

The thiuret ion is essentially planar, and nearly symmetric about an axis through the cyclic nitrogen atom and the midpoint of the sulphur-sulphur bond. The bond lengths show that the ion is stabilized through π -orbital delocalization, the conjugation being most pronounced in the carbon-nitrogen part of the ion.

In the crystal, both sulphur atoms of the disulphide group form close contacts (3.315 and 3.272 \pm 0.004 Å) with the same chloride ion, and the indicated bonding may be explained in terms of three-

center two-electron bonds.

The linear X···S-S···X arrangement which was found in crystals of thiuret hydrociodide and hydrobromide is also present in crystals of thiuret hydrochloride hemihydrate. In the latter compound the chlorine-sulphur distances in this arrangement, are 3.864 ± 0.004 Å and 3.527 ± 0.004 Å, and the interaction between halogen and sulphur is weaker than in thiuret hydroiodide and hydrobromide.

The following hydrogen bonds occur in the crystal, N-H···O = 2.870 ± 0.010 Å N-H···N = 3.000 ± 0.010 Å, N-H···Cl = 3.114 and 3.132 ± 0.007 Å, and O-H···Cl = 3.156 ± 0.007 Å

0.006 Å.

The unsaturated five-membered disulphide ring of the thiuret ion (I) possesses a sextet of π -electrons and is pseudo-aromatic. While the disulphide group is normally non-planar, with a dihedral angle of about 90° between the planes

of the valences of the two sulphur atoms,¹ it has been found to be planar in unsaturated five-membered cyclic disulphides.²⁻⁸ Foss ² has suggested that the stability of the planar disulphide group in these compounds is due to π -bonding in which π -electrons on the sulphur atoms participate. Support for this idea derives from structure investigations of a series of compounds containing an unsaturated five-membered disulphide ring.²⁻⁸ The lengths of the cyclic carbon-sulphur bonds in these compounds are found within the range 1.67-1.78 Å, and the reported values for the sulphur-sulphur bond lengths varies from 2.00 to 2.09 Å.

The conjugation in the carbon-sulphur part of an unsaturated five-membered disulphide ring is most pronounced when the substituents to the ring do not, or only to a small degree, take part in π -bonding with ring atoms. In mono-phenyl substituted 1,2-dithiolium ions, for example,^{6,9} the sulphur-sulphur bond length has been found to be 2.00-2.03 Å and the carbon-sulphur bond lengths 1.67-1.71 Å. These values agree, if one assumes a linear relationship bond-order/bond-length, with the bond orders, calculated by Bergson,¹⁰ for the S—S and C—S bonds in the unsaturated 1,2-dithiolium ion. Xanthan hydride and rhodan hydrate, on the other hand, have sulphur-sulphur and carbon-sulphur bond lengths of about 2.06 Å and 1.76 -1.78 Å, respectively.^{4,5} In the latter compounds the cyclic carbon atoms, bonded to the disulphide group, strongly engage in π -bonding with external atoms, at the expense of the conjugation in the carbon-sulphur part of the ring.

In the unsaturated five-membered cyclic disulphide, 4-methyl-trithione, only one of the carbon atoms, bonded to the disulphide group is engaged in π -bonding with an external atom.³ Thus, according to the above, one might expect the conjugation in the disulphide group of this compound, to be somewhat more pronounced than in xanthan hydride and rhodan hydrate. The length of the C—S bond on the thione side of the disulphide ring in 4-methyl-trithione is 1.747 ± 0.017 Å and the length of the C—S bond on the other side of the ring is 1.713 ± 0.017 Å. Furthermore, the length of the sulphur-sulphur bond is reported to be 2.047 ± 0.007 Å, and Jeffrey and Shiono³ conclude that this sulphur-sulphur bond is a pure single bond. The present authors believe that the mentioned sulphur-sulphur bond has some double bond character and that 4-methyl-trithione, from what has been said above, and as far as the conjugation in the disulphide group concerns, may be regarded as intermediate between the 1,2-dithiolium ion on one side, and xanthan hydride and rhodan hydrate on the other. Bergson ¹⁰ has calculated the π -bond order of the sulphur-sulphur bond in 4-methyl-trithione to be 0.242.

The question whether and to which degree the close contacts between halogen and sulphur, found in crystals of thiuret hydroiodide² and hydrobromide,⁸ affects the sulphur-sulphur bond, incited the present investigation of thiuret hydrochloride hemihydrate. The close contacts occur in approximately linear X···S—S···X arrangements, and may influence the length of

the sulphur-sulphur bond through transfer of charge from the halide ion to those p-orbitals of sulphur already engaged in the sulphur-sulphur σ -bond. One may expect the strength of this partial bonding to decrease with increasing electronegativity of the halide ion, and whether it affects the length of the sulphur-sulphur bond in thiuret hydroiodide and hydrobromide might therefore be revealed through a structure investigation of thiuret hydrochloride hemihydrate.

EXPERIMENTAL

The unit cell and space group of thiuret hydrochloride hemihydrate have been reported by Foss.¹¹ The crystals are monoclinic, with the unit cell dimensions (redetermined): a=19.53 Å, b=5.47 Å, c=14.31 Å, and $\beta=114.5^\circ$. The experimental error is estimated to be within 0.2 %.

There are eight formula units per unit cell and the space group is C2/c.

The intensities of the h0l, h1l, h2l, h3l, and hk0 reflections were estimated by eye from sets of Weissenberg photographs, taken with $CuK\alpha$ radiation. A crystal with cross-section 0.16×0.27 mm was used for the recordings around the b axis; for the hk0-recordings a crystal with cross-section 0.3×0.08 mm was used. 852 independent reflections were obtained and measured. The intensities were corrected for Lorentz and polarization effects but not for absorption. Common reflections in h0l, h1l, h2l, h3l, and hk0 were used to put all the reflections on the same scale.

The calculated structure factors in Table 12 are based on the atomic scattering curves for chloride ion, sulphur, oxygen, nitrogen, carbon and hydrogen which are given in the *International Tables*, the first set of the listed scattering factors for carbon being used.

STRUCTURE DETERMINATION

Direct solution. The structure was solved in the b-axis projection by means of Harker Kasper inequalities and systematic use of Sayre's equation, and a brief account of this has been reported earlier. A more detailed description of the procedure is given here.

Observed hol structure factors were put on an absolute scale by means of Wilson's method, ¹³ and unitary structure factors were calculated for the strongest reflections. The u-values, found in this way, later proved to be about

30 % too high.

The signs for 406 and $14,0,\overline{14}$ were chosen positive, and combination of these two reflections in a Harker Kasper inequality gave the sign for $18,0,\overline{8}$. The signs for 12,0,4, 10,0,0, $12,0,\overline{2}$, and $12,0,\overline{12}$ were denoted a,b,c, and d, respectively, and sixteen sets of probable signs were derived, by means of Sayre's equation $S_h \cdot S_{h'} \approx S_{h+h'}$, for the 37 reflections in Table 1. This could be reduced to four sets of probable signs by taking into account the derived relationships between b,c, and d; see for instance derived signs for $10,0,0,80\overline{8}$ and $12,0,\overline{12}$ in Table 1. Furthermore, one of the remaining four sign sets could be regarded as unlikely because it had all signs positive.

Fourier maps corresponding to the three sets of probable signs were computed, and the molecule was recognized in one of them. This Fourier map, shown in Fig. 1, has a = +, b = c = -, and d = +, and all derived signs

later proved to be correct.

Table 1.	Unitary	structure	factors	and	probable	signs	for	the	h0l	reflections	used	in t	the
	•				cture dete								

h	l	100u	sign	h	l	100u	sign
0	16	42	ad	2	8	37	bc
10	0	90	b, dc	4	8	63	\boldsymbol{a}
16	0	42	abd	8	-8	78	b, c
2	2	36	ab	14	-8	51	abd
8	-2	65	\boldsymbol{a}	18	-8	84	+
12	-2	68	$oldsymbol{c}$	24	-8	73	ad
18	-2	37	ab	16	-10	65	ab
22	2	63	bc	20	-10	50	bc
2	4	56	ab	4	12	42	ab
6	4	38	bc, d	2	12	46	\boldsymbol{c}
12	4	106	\boldsymbol{a}	6	-12	40	\boldsymbol{a}
16	4	49	$oldsymbol{c}$	12	-12	72	d, $+$
4	-4	49	bd	22	-12	41	bd
20	-4	71	ac	4	14	78	b
4	6	84	+	10	— 14	47	abd
14	6	60	\boldsymbol{b}	14	-14	78	+
6	-6	43	b, c	20	-14	76	ad
10	-6	38	abc	10	16	36	abd
16	-6	50	d				

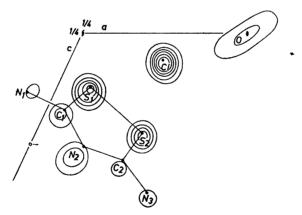


Fig. 1. Fourier map of thiuret hydrochloride hemihydrate in the b-axis projection, based on the 37 reflections in Table 1. with a=+, b=c=- and d=+. Contours at arbitrary but equal intervals.

Structure refinement. The y-coordinates for the atoms in the thiuret ion were estimated by taking into account that the thiuret ions, as indicated by the b-projection, were arranged in pairs over centers of symmetry through N—H···N hydrogen bonds of length about 3.0 Å. Such an arrangement of thiuret ions was found in thiuret hydrobromide, the N—H···N distance there being 3.07 Å. Furthermore, an approximately linear Cl···S—S···Cl arrangement was assumed, from the X···S—S···X arrangements found in thiuret hydroiodide and hydrobromide. The y-coordinate of the water oxygen on the

twofold axes was estimated by assuming that there probably would be hydrogen bonds between the oxygen atom and two chloride ions.

The structure was refined by least squares methods on an IBM $1620^{\text{ II}}$ computer, using a program designed by Mair. 14 Weighting scheme No. 3, recommended by Mair, was used with a = 12 and b = 7.5. The refinement comprises the hol, hll, h2l, h3l, and hk0 reflections, and was carried out with anisotropic temperature factors for all atoms except the hydrogens, which were given isotropic temperature factors. Final value of the agreement factor $R = \sum ||F_0| - |F_c||/\sum |F_0|$ is 0.059. Eight low order reflections, supposed to

Table 2.	Final aton	ic coordinates	from the	e least s	quares	refinement.

Atom	\boldsymbol{x}	$oldsymbol{y}$	\boldsymbol{z}
Cl	0.11067	0.25841	0.18718
$\mathbf{S_1}$	0.20221	0.81731	0.12798
S.	0.09096	0.81664	0.02381
$\mathbf{S_2}$ $\mathbf{N_1}$	0.2923	0.4716	0.1136
N_2	0.1697	0.4463	-0.0077
N_s	0.0426	0.4605	-0.1121
$\mathbf{C_i}$	0.2232	0.5545	0.0736
$\tilde{\mathbf{C}}_{2}^{1}$	0.1016	0.5517	-0.0383
o'	0.0000	-0.0513	0.2500
$\mathbf{H_1}$	0.299	0.336	0.093
H.	0.323	0.530	0.178
$\mathbf{H_{2}^{'}}$ $\mathbf{H_{3}^{'}}$	0.047	0.358	-0.147
$\widetilde{\mathbf{H}}_{4}^{3}$	-0.003	0.521	-0.133
$\widetilde{\mathbf{H}}_{5}^{4}$	-0.030	0.047	0.250

Table 3. Components of atomic vibration tensors Ur in Å2, referred to crystallographic

Atom	U_{11}	$oldsymbol{U_{22}}$	$oldsymbol{U_{33}}$	$U_{\scriptscriptstyle 12}$	$oldsymbol{U_{23}}$	$oldsymbol{U_{31}}$
Cl	0.0348	0.0632	0.0453	0.0133	0.0128	0.0178
$\mathbf{S_1}$	0.0348	0.0509	0.0376	0.0023	-0.0084	0.0148
\mathbf{S}_{\bullet}^{T}	0.0333	0.0525	0.0433	0.0085	-0.0017	0.0161
$egin{array}{c} \mathbf{S_2} \\ \mathbf{N_1} \\ \mathbf{N_2} \\ \mathbf{N_3} \end{array}$	0.0330	0.0595	0.0397	0.0069	-0.0131	0.0071
N,	0.0296	0.0446	0.0350	0.0043	-0.0011	0.0128
N_3	0.0271	0.0648	0.0439	0.0058	-0.0041	0.0069
$\mathbf{C_i}$	0.0292	0.0619	0.0297	0.0008	0.0014	0.0153
C_2	0.0292	0.0532	0.0338	0.0029	0.0012	0.0134
o o	0.0488	0.0606	0.0571	0.0000	0.0000	0.0251

Final B-values, in the expression exp $[-B(\sin^2\theta/\lambda^2)]$ for the hydrogen atoms $H_1...H_s$, are -0.1, 0.7, 1.9, 1.7, and 1.8 $^{\text{A}^2}$, respectively.

be affected by secondary extinction, were excluded from the least squares refinement. These reflections, marked with asterisks in Table 12, were included in the final structure calculations with $F_{\rm o}=F_{\rm c}$. Atomic coordinates and components of atomic vibration tensors ${\bf U}^{\rm r}$ are

given in Tables 2 and 3. The observed and calculated structure factors are

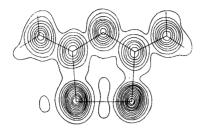


Fig. 2. Electron density map of the thiuret ion, showing the electron density in the plane of the ion. Contour intervals for carbon and nitrogen 1 e.Å⁻³ and for sulphur 2 e.Å⁻³. Lowest contour at 1 e.Å⁻³.

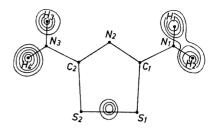


Fig. 3. Electron density map in the plane of the thiuret ion with all atoms but the hydrogens subtracted. Contour intervals of 0.1 e.Å⁻³ starting at 0.3 e.Å⁻³.

listed in Table 12. An electron density map, showing the electron density in the plane of the thiuret ion is given in Fig. 2, and a corresponding electron density map with all atoms except the hydrogens subtracted is given in Fig. 3.

Thermal analysis. Cruickshank ¹⁵ has shown how the libration and translation of a rigid molecule can be deduced from the anisotropic thermal vibrations of its different atoms. The method presupposes that the axes of libration intersect in a known point, such as a center of symmetry. Hirshfeld ¹⁶ suggests that the libration centre can not, in most cases, be located a priori, and has modified Cruickshank's method accordingly.

The computer program used in the rigid-body calculations referred to below is written in FORTRAN II by Hirshfeld, and the calculations were carried out on the IBM $1620^{\text{ II}}$.

An orthogonal molecular coordinate system L, M, N was chosen such that L and M are in the plane of the thiuret ion and N perpendicular to this plane. The origin is in an approximate center of gravity and the directions of L, M, and N are the directions of the principal axes of inertia. The direction cosines of L, M, and N with respect to the crystallographic axes are given in Table 4 together with the coordinates of the origin.

Coordinates and vibration tensors of the atoms in the thiuret ion (except hydrogen), were transformed to the molecular coordinate system, and the transformed values are given in Tables 5a and 6.

The rigid-body parameters of the thiuret ion were calculated according to Hirshfeld's procedure, 16 with triple weight on the sulphur atoms, and the final values of the translation and libration parameters are given in Table 7. Components of atomic vibration tensors as calculated from the rigid-body parameters are listed in Table 6. Principal components of the rigid-body vibrations and their direction cosines with respect to molecular axes together with the coordinates of the libration center are given in Table 8.

The coordinates of the atoms in the thiuret ion were corrected for rigid-body libration according to Cruickshank's method.¹⁷ The corrected coordinates are listed in Table 5b.

Table 4. Origin, and direction cosines of the axes L, M, N of the molecular coordinate system, referred to crystal axes.

	a	\boldsymbol{b}	$oldsymbol{c}$
$oldsymbol{L}$	-0.7631	-0.0085	-0.2716
M	-0.3724	0.8230	0.5448
N	-0.5282	-0.5680	0.7934

Origin at x = 0.1553, y = 0.6715, z = 0.0441

Table 5. Atomic coordinates in the coordinate system $L,\,M,\,N\,$ (a) final coordinates from the least squares refinement, (b) the latter values corrected for rigid-body libration.

		(a)			(b)	
Atom	L (Å)	M (Å)	N (Å)	L (Å)	M (Å)	N (Å)
$\mathbf{S_1}$	-1.031	0.970	0.016	-1.035	0.975	0.016
$\mathbf{S_2}$	1.031	0.964	-0.017	1.035	0.969	-0.017
$\mathbf{N}_{\mathtt{1}}$	-2.302	-1.345	-0.002	-2.311	1.356	-0.001
N_2	-0.002	-1.521	-0.035	-0.002	-1.524	-0.035
N_3	2.298	-1.347	0.046	2.306	-1.349	0.046
$\mathbf{C_1}$	-1.120	-0.789	0.000	-1.124	-0.790	0.000
C_2	1.127	-0.790	-0.008	1.131	-0.790	-0.008

Table 6. Components of atomic vibration tensors V^r in $Å^2$ as found by the least squares refinement (exp) and as calculated from the rigid-body parameters (RB).

Atom	V_{LL}	V_{MM}	V_{NN}	$V_{L\dot{M}}$	V_{MN}	V_{LN}
$S_1 (exp) (RB)$	$0.0352 \\ 0.0342$	$0.0367 \\ 0.0407$	$0.0515 \\ 0.0511$	$-0.0002 \\ -0.0011$	-0.0100 -0.0099	$-0.0011 \\ -0.0008$
S_2 (exp) (RB)	$0.0354 \\ 0.0342$	$0.0413 \\ 0.0407$	$0.0520 \\ 0.0529$	$-0.0082 \\ -0.0061$	$-0.0080 \\ -0.0087$	$0.0000 \\ 0.0003$
$N_1(\exp) \ (RB)$	$0.0303 \\ 0.0311$	$0.0390 \\ 0.0471$	$0.0708 \\ 0.0681$	$-0.0003 \\ -0.0061$	$-0.0108 \\ -0.0103$	$0.0032 \\ 0.0003$
$egin{aligned} \mathbf{N_2}(\mathbf{exp}) \ (\mathbf{RB}) \end{aligned}$	$0.0304 \\ 0.0315$	$0.0374 \\ 0.0390$	$0.0419 \\ 0.0367$	$-0.0039 \\ -0.0036$	$-0.0060 \\ -0.0094$	$0.0002 \\ 0.0000$
$N_3(\exp) \ (RB)$	$0.0264 \\ 0.0311$	$0.0528 \\ 0.0470$	$0.0643 \\ 0.0655$	$-0.0045 \\ -0.0010$	$-0.0087 \\ -0.0111$	$0.0003 \\ -0.0006$
$^{\mathrm{C_3}\mathrm{(exp)}}_{\mathrm{(RB)}}$	$0.0308 \\ 0.0304$	$0.0508 \\ 0.0410$	$0.0360 \\ 0.0403$	$-0.0024 \\ -0.0039$	$-0.0169 \\ -0.0095$	$-0.0011 \\ 0.0002$
$^{\mathrm{C_2}}\left(\mathrm{exp} \right) \ \mathrm{(RB)}$	$0.0303 \\ 0.0304$	$0.0457 \\ 0.0410$	$0.0398 \\ 0.0400$	$-0.0037 \\ -0.0033$	-0.0099 -0.0096	$-0.0002 \\ 0.0004$

Table 7. Final rigid-body translation parameters T_{ij} and libration parameters ω_{ij} .

	LL	MM	NN	LM	MN	LN	
T (Å)	0.03036	0.03908	0.03250	-0.00364	-0.00922	0.00032	
ω (rad ²)	0.005221	0.005967	0.001528	-0.000310	-0.000287	0.000270	

Table 8. Principal components of rigid-body vibrations, with direction cosines, and coordinates of libration centre, referred to molecular axes.

	$oldsymbol{L}$	$m{M}$	N
$T_1{}^2 = 0.0462 \text{ Å}^2$	0.1971	-0.9081	-0.3693
$T_{2}^{-2} = 0.0304$	-0.8114	0.0603	-0.5813
$T_{3}^{-2}=0.0252$	0.5502	0.4143	-0.7249
$\omega_1^2 = 0.0060 \mathrm{rad}^2$	-0.3258	0.9421	0.0779
$\omega_2^2 = 0.0051$	0.9445	0.3209	0.0691
$\omega_{3}^{2} = 0.0014$	0.0400	0.0961	-0.9945

Libration centre at L = 0.005, M = 0.622, N = 0.021.

The amplitudes of translational motion in directions of the principal axes are, according to the values in Table 8, 0.16, 0.18, and 0.22 Å, and the amplitudes of libration about principal axes are 2.1, 4.1, and 4.4°. The libration center lies 0.62 Å off the origin of the molecular coordinate system in direction towards N_2 . Minimum libration occurs about an axis through this center and approximately perpendicular to the molecular plane. The libration amplitudes around the two other principal axes are nearly equal, 4.1 and 4.4°, and the axes lie nearly in the plane of the molecule, roughly parallel to M and L, respectively.

Table 9. Bond lengths (l) and standard deviation in bond lengths $\sigma(l)$ in the thiuret ion; values in parenthesis are without correction for rigid-body libration.

Bond	l (Å)	$\sigma\left(l ight)\left(m \AA ight)$
$\begin{array}{c} S_1 - S_2 \\ S_1 - C_1 \\ S_2 - C_3 \\ C_1 - N_2 \\ C_2 - N_2 \\ C_1 - N_1 \\ C_2 - N_3 \end{array}$	$\begin{array}{ccc} 2.071 & (2.063) \\ 1.767 & (1.761) \\ 1.762 & (1.756) \\ 1.342 & (1.337) \\ 1.350 & (1.345) \\ 1.315 & (1.310) \\ 1.303 & (1.298) \end{array}$	0.004 0.007 0.007 0.010 0.009 0.009 0.010
$egin{array}{c} N_1-H_1 \ N_1-H_2 \ N_3-H_3 \ N_3-H_4 \ \end{array}$	0.83 0.93 0.77 0.89	0.1 0.1 0.1 0.1

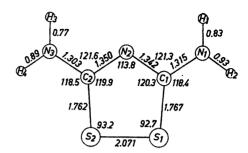


Fig. 4. Bond lengths (Å) and bond angles (°) in the thiuret ion.

Table 10. Bond angles and standard deviation in bond angles in the thiuret ion; values in parenthesis are without correction for rigid-body libration.

	\mathbf{Angle} (°)	σ (°)
$C_1 - S_1 - S_2$	92.7 (92.7)	0.3
$S_1-C_1-N_2$	120.3 (120.3)	0.5
$S_1 - C_1 - N_1$	118.4 (118.4)	0.6
$\mathbf{N_1} - \mathbf{C_1} - \mathbf{N_2}$	121.3 (121.3)	0.6
$C_1-N_2-C_2$	113.8 (113.8)	0.6
$S_2-C_2-N_2$	119.9 (119.8)	0.5
$S_2 - C_2 - N_3$	118.5 (118.5)	0.5
$\vec{N_2} - \vec{C_2} - \vec{N_3}$	121.6 (121.7)	0.6
$S_1-S_2-C_2$	93.2 (93.3)	0.3

DISCUSSION

The thiuret ion. Bond lengths as calculated from the coordinates in Table 5b, are listed in Table 9 and shown in Fig. 4. An assumed 0.1 % standard deviation in cell dimensions has been included in the listed standard deviation in bond lengths. Bond angles calculated from the coordinates in Table 5b are listed in Table 10 and shown in Fig. 4.

The thiuret ion is essentially planar; the equation for the least squares plane of the molecule, excluding the hydrogen atoms and with double weight on the sulphur atoms is

$$-10.3164x - 3.1068y + 11.3535z = -3.1888$$

where x, y, and z are the fractional coordinates with respect to the crystallographic axes. The N-coordinates in Table 5 give the distances of different atoms from the molecular plane, and show that S_1 , S_2 , N_2 , and N_3 probably are slightly out of the plane.

A least squares plane for the atoms of the five-membered ring was then calculated with triple weight on the sulphur atoms. The distances in Å of the different atoms in the thiuret ion from this plane are S_1 (0.003), S_2 (-0.005), C_1 (0.001), C_2 (0.020), N_1 (-0.009), N_2 (-0.015), and N_3 (0.094). The five-membered ring is thus planar within the error; one of the exocyclic nitrogen atoms (N_1) lies in the plane, while the other (N_3) lies significantly out of the plane by 0.094 Å.

In thiuret hydrobromide the thiuret ion is found to be planar.⁸ For thiuret hydroiodide a non-planar disulphide ring is indicated ² but this is probably

related to the uncertainty of the atomic coordinates of carbon and nitrogen in the structure.

Bond lengths and angles, cf. Fig. 4, show that in thiuret hydrochloride hemihydrate an approximate mirror plane occurs perpendicular to the molecular plane and through N_2 and the midpoint of the sulphur-sulphur bond. Such a mirror plane is crystallographically required in thiuret hydroiodide. Bond lengths and bond angles in the thiuret ion, as found in the present investigation, deviate by less than one standard deviation from corresponding bond lengths and angles in the symmetric model arrived at by averaging the dimensions of the two halves of the ion.

The slight difference in bond lengths between cyclic and exocyclic carbon-nitrogen bonds found for thiuret hydrochloride hemihydrate is probably significant. Thus the average length of cyclic C—N bonds is 1.346 Å and of exocyclic C—N bonds 1.309 Å. By assuming the thiuret ion to be symmetric, the corresponding standard deviation in C—N bond lengths becomes 0.007 Å, and the difference between cyclic and exocyclic C—N bond lengths is then more than five times this figure. The value 1.346 \pm 0.007 Å for the cyclic C—N bond lengths agrees with the aromatic C—N bond length, 1.340 Å, found in pyridine. In the unsaturated five-membered cyclic disulphide xanthan hydride, the average value of cyclic C—N bond lengths is 1.343 \pm 0.011 Å, and also in this compound the exocyclic C—N bond is found to be shorter, 1.307 \pm 0.011 Å, than the cyclic C—N bond. The latter C—N bond lengths are not corrected for rigid-body libration, and are as should be expected, somewhat smaller than the corrected values for thiuret hydrochloride hemihydrate.

The carbon-sulphur bonds in thiuret hydrochloride hemihydrate, 1.762 and 1.767 \pm 0.007 Å, are shorter than single bonds. This is clearly seen through a comparison with the saturated five-membered cyclic disulphide, 1,2-dithiolane-4-carboxylic acid, 18 where the C-S bonds are found to be 1.83 and 1.85 ± 0.02 Å. Even if the carbon atoms bonded to sulphur in the latter compound are mainly sp^3 -hybridized, and one thus might expect the C-S single bond length to be somewhat smaller in the thiuret ion than in 1,2-dithiolane-4-carboxylic acid, the observed difference in C-S bond lengths in the two compounds, 0.07 Å, is hardly due to the greater s-character of the bonding orbital on the carbon atoms in the thiuret ion only. According to the bond-length/bond-order relationship for a C-S bond, proposed by Abrahams, 19 a C-S bond of 1.76 Å corresponds to a π -bond order of about 0.4.

The length of the sulphur-sulphur bond in thiuret hydrochloride hemihydrate is found to be 2.071 ± 0.004 Å. This value includes correction for rigid-body libration; the uncorrected value is 2.063 Å. In thiuret hydrobromide ⁸ and hydroiodide, ² where corrections for rigid-body libration were not undertaken, the sulphur-sulphur bond lengths are 2.081 ± 0.009 and 2.088 ± 0.012 Å, respectively. A least squares refinement of the thiuret hydroiodide structure ⁷ gave for the sulphur-sulphur bond a length of 2.083 ± 0.015 Å. There is thus no significant difference between the sulphur-sulphur bond lengths as found in the three thiuret hydrohalides, but the observed differences may be real, as discussed below.

Although the sulphur-sulphur bond length in thiuret hydrochloride hemihydrate, 2.071 ± 0.004 Å, has been found smaller than the accepted value 2.08 Å for a sulphur-sulphur single bond, it does not differ significantly from this value. This implies that the sulphur-sulphur bond in thiuret hydrochloride hemihydrate might be accepted as a pure single bond, or close to. It seems likely, however, that a query should be put at the well known value 2.08 Å. As regards cyclic disulphides, it seems justified to suggest a somewhat longer single bond length. The value 2.10 Å, is from a consideration of available experimental data, by one of the authors proposed as a more relevant bond length for a single bond between the two divalent sulphur atoms of a cis planar disulphide group. Since this value, 2.10 Å, emerges from data uncorrected for rigid-body libration, it seems justified to compare the uncorrected sulphur-sulphur bond length, 2.063 Å, in thiuret hydrochloride hemihydrate with it when judging about the double bond character of this bond. It therefore seems likely that the conjugation in the thiuret ion also extends over the sulphur-sulphur bond.

The environment of the disulphide group. The environment of the disulphide group in the crystals of thiuret hydrochloride hemihydrate is shown in Fig. 5, and the corresponding interatomic distances and angles are listed in Table 11. The values are based on the coordinates in Table 1.

The sum of van der Waals radii for chlorine and sulphur is 3.65 Å, according to the values given by Pauling, 21 and thus Fig. 5 shows that the sulphur atoms of the disulphide group form three close contacts with two neighbouring chloride ions. In thiuret hydroiodide and hydrobromide there are, as mentioned in the introduction, close contacts between halogen and sulphur in a linear X ··S—S···X arrangement. A similar arrangement, with chlorine-sulphur distances 3.864 and 3.527 \pm 0.004 Å, occurs in crystals of thiuret hydrochloride hemihydrate. One of the latter distances is slightly shorter than the corresponding van der Waals contact and may indicate a weak bond. However, this partial bonding of σ -bond order about 0.10, is probably too weak to affect the sulphur-sulphur bond length. In thiuret hydrobromide and hydro-

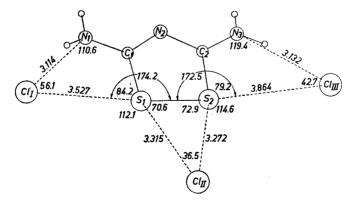


Fig. 5. Atomic distances and angles with reference to the environment of the disulphide group.

Table 11. Atomic distances and angles with reference to the environment of the disulphide group, together with the respective standard deviations in atomic distances and angles.

	Distance (Å)	σ (Å)
S_1 Cl_T	3.527	0.004
\mathbf{S}_{1}^{1} \mathbf{Cl}_{11}^{1}	3.315	0.004
$S_2 \cdots Cl_{TT}$	3.272	0.004
$S_2 \cdots Cl_{III}$	3.864	0.004
$N_1 \cdots Cl_r$	3.114	0.007
N_3 Cl_{III}	3.132	0.007
	Angle (°)	σ (°)
$Cl_1 \cdots N_1 - C_1$	110.6	0.5
$Cl_1S_1-C_1$	84.2	0.3
$Cl_1 \cdots S_1 - S_2$	174.2	0.2
$Cl_1 \cdots S_1 \cdots Cl_{II}$	112.1	0.2
$S_1 \cdots Cl_1 \cdots N_1$	56.1	0.3
$Cl_1 \cdots S_1 - S_2$	70.6	0.3
$Cl_{II}S_2-S_1$	72.9	0.3
Cl _{II} S ₂ Cl _{III}	114.6	0.2
$S_1 \cdots Cl_{11} \cdots S_2$	36.5	0.2
$Cl_{11}\tilde{S}_{2}-\tilde{S}_{1}$	172.5	0.2
$Cl_{III}S_2-C_2$	79.2	0.3
$Cl_{111}^{}N_s-C_s$	119.4	0.5
S_2 Cl_{III} N_3	42.7	0.3

'odide the partial sulphur-halogen bonding in the linear X...S.—S...X arrangement, equally strong on either side of the disulphide group, corresponds to a σ -bond order of about 0.23. The sulphur-sulphur bonds in the latter compounds are found to be 0.02 Å longer than in thiuret hydrochloride hemi-hydrate. The difference in bond length, although not significant, seems to indicate that the partial bonding between halogen and sulphur in crystals of thiuret hydroiodide and hydrobromide have caused a small lengthening of the sulphur-sulphur bond in those compounds.

Beside the sulphur-chlorine close contact discussed above, the sulphur atoms of the disulphide group in crystals of thiuret hydrochloride hemihydrate form two close contacts with a second chloride ion. This chloride ion lies close to the normal to the sulphur-sulphur bond through its midpoint, 0.22 Å from the plane of the thiuret ion; the sulphur-chlorine distances are 3.315 and 3.272 ± 0.004 Å. A similar arrangement occurs in crystals of thiuret hydrobromide and also in crystals of 3-phenyl-1,2-dithiolium iodide. These halogen-sulphur-sulphur configurations are probably established through overlap of one filled orbital on the halogen ion with two orbitals of the sulphur atoms, one from each. Because both sulphur atoms form weak bonds with halogen, one may assume that charge is partially transferred from the halogen ion to the sulphur atoms, e.g. to those p-orbitals on the sulphur atoms already engaged in the sulphur-carbon σ -bonds, with weak three-center two-electron bonds as result.

The b-axis projection of the crystal structure of thiuret hydrochloride is shown in Fig. 6. The thiuret ions are arranged in pairs over centers of symmetry through $N-H\cdots N$ hydrogen bonds of length 3.000 ± 0.010 Å. The

Table 12. Observed and calculated h0l, h1l, h2l, h3l, and hk0 structure factors for thiuret hydrochloride hemihydrate. The values given are 25 times the absolute values.

h	k	1		ъ	h	k	1	Fo	Pc	h	k	1	Po	F _c	h i	k 1 F _o F _c	
0	0	2	F ₀ 2389	F _C 2639	6	o	8	^o 635	715	11	1	0	1045	1051	5	1 + 2 1258 +1192	
0	0	4	772 1727	- 745 1809	8	0	8	945 616	- 935 559	13 15	1	0	< 184 1189	92 1126	5	1 - 4 2006 -1917	
0	0	8	898	1541 859	12	0	8	401 490	- 374 439	17 19	1	0	974 < 180	- 916 118	5	1 - 5 4191 4090 1 - 6 1622 -1522 1 - 7 854 759	
0	0	12	846 590	- 872 - 641	2	0	- 8	◄ 192	200	21	1	0	< 190	172	5	1 - 8 641 599	
U	0	16	652	631	6	0	- 8 - 8	3208 2319	2884 2168		1	2	999	1174 - 983 2977	5	1 -9 1057 936 1 -10 < 211 - 65 1 -11 405 307	
2	0	0	947 1818	-1082 -2019	8 10 12	0	- 8 - 8	3779 < 207 532	-3677 158 513	į	1	3 4 5	2894 772 530	809 - 494	5	1 -12 625 - 536 1 -13 722 688	
6 8	0	0	2143 877	-2123 - 719	14	0	- 8 - 8	1758 525	1640 517		1	6	352 718	- 315 698	5	1 -14 530 - 545 1 -15 1173 1100	
12	0	000	4387 1047 794	4631 - 977 - 803	16 18 20	0	- 8 - 8	2246 < 240	-2135	i	i	7 8 9	751 2315	- 680 2371	5	1 -16 < 184 46	
16	0	0	1187	-1165 36Z	22 24	0	- 8	< 209 1119	136 97 1234	į	i	10 11	1148	-1154 - 659	7	1 2010 -2076	
18 20 22	0	0	1034	1033	2	0	10	300	- 236	į	i	12	< 234 < 223	- 97 84	7	1 Z 1204 -1173 1 3 4035 -4382	
2	0	ż	3411	-3599	4	0	10	352 631	- 322 - 634		i	14	< 201 490	- 43 568	7	1 4 873 849 1 5 542 540	
4	0	2	401 656	471 - 688	10	0	10	507 616	525 596	1	1	16	< 116	- 50	7 7	1 6 < 215 135 1 7 467 - 455	
8 10	0	2 2 2	904 294	902	12	0	10	379	- 340	1	i	- 1 - 2	2807 1278	2920* -1305	7 7 7	1 8 < 234 - 142 1 9 989 - 985 1 10 319 - 232	
12	0	z	310 395	319 372	2	0	-10	< 228 1206	-1120	1	- -	- 3 - 4 - 5	1034 879	- 993 951	7 7 7.	1 10 319 - 232 1 11 412 - 312 1 12 436 381	
16	0	2 2 2	1479 327	-1485 - 350 - 333	6 8 10	0	-10	724 929	650 - 943 -1334	1	1	- 6	2856 153	-2782 50 -2081	7	1 13 145 - 221	
20	0		341	- 333 1795	12	00	-10 -10	1336 < 240 759	47 - 745	-	į	- 7 - 8	2037 1287 1171	1362	7	1 - 1 980 1054	
2 4 6	0 -	- z	2058 3018 2679	-2804 -2682	16	0	-10	1857 285	1789	į	i	-10	683	655 -1802	7 7 7	1 - 3 2164 -2128	
8	0 -	- Z	5297 956	-5357° 869	20 22	0	-10		-1139 - 164	į	1	-12 -13	374 < 232	36Z - 165	7	1 - 5 358 - 335	
12	۰ -	- 2 - 2 - 2	3030 362	2833 - 311	24	0	-10	215	231	1	i	-14 -15	< 217 372	- 56 - 352	7 7 7	1 - 7 507 - 467 1 - 8 2015 -1905	
16.	0 +	 2	1117 947	-110i - 947	2	0	12	455 941	- 435 - 925	1	1	-16	< 151	37	7	1 - 9 751 656 1 -10 707 - 636 1 -11 1539 1500	
20 22	0 -	- Z	453 1094	468 1153	6 8	0	12	1256 958	919	3	!	2	391 1406	390 -1477	7 7 7	-	
2	0	4	4664	4732*	10 2	0	12 -12	443 1316	- 450 1320	3	i	3 4 5	2499 1187 956	2725 1150 907	7 7	1 -14 < 230 - 112 1 -15 581 616	
6	0	4	2405 2042 1113	-2380 -2060 1213	4	0	-12.	1224	1327	3	i	6 7	296 1406	- 320 1349	7	1 -16 < 192 21	
10	0	4	697	689 3455	8	0	-12 -12	430	- 38Z -127Z	3	į	8 9	741 838	~ 707 - 848	9	1 1 2828 -2860	
14	0	4	1438	-1486 -1108	12	0	-12 -12	2056 459	2089 436	3	İ	10	395 565	- 408 - 584	9 9	1 2 246 237 1 3 763 725	
18	ŏ	4	< 190	175	16 18	0	-12	285 550	- 255 581	3	1	12	< 227 685	216 673	9	4 < 256 67 5 292 316	
2	0 .	- 4 - 4	1026 4360	984 -3996	20 22	0	-12 -12	941 680	- 998 748	3	1	15	< 178 546	- 639	9 9	1 6 641 670 1 7 1586 -1673 1 8 1384 1483	
8	0 -	- 4	958 2372	919 2277	2	0	14	408	- 329 - 185	.3 3	ı	- 1 - 2	333	288 ·2548	9	1 9 449 473	
10	ō.	- 4	1334 2364	-1349 2369	6	0	14	223 540	545	3 3.	i L	- 2 - 3 - 4	2739 6836 5353	7353 5594	ģ	1 11 407 404	
14 16 18	0 -	- 4 - 4	277 546 438	270 519 416	2	0	-14 -14	9 93 1764	- 923 1615	3. 3 3	i	- 5	< 132 972	- 10 915	9	1 - 1 1475 -1391	
20 22	ο.	- 4 - 4	1688	-1579 581	6	0	-14	401 511	353 - 476	3	į	- 7 - 8	527 203	- 559 - 213	9	1 - 2 250 100	
24		- 4	391	463	10	0	-14	1198 443	-! 184 - 427	3	İ	- 9 -10	1566 213	1565 138	9	1 - 4 252 - 238 1 - 5 840 - 783	
2	0	6	1063 4788	-1118 -4838	14	0	- (4. - 14	1862	1714	3	1	-11 -12	< 376 1187	- 68 1188	9	1 - 6 474 - 427 1 - 7 < 182 - 54 1 - 8 1020 943	
6 8	0	6	217 550	280 600	18 20	0	-14 -14	256 1305	- 205 -1345	3	ŀ	-13 -14	< 234 542	- 122 - 563	9 9 9	-8 1020 943 -9 2532 -2410 -10 < 215 -59	
12	0	6	575 364	561 363	2	0	-16	< !82	- 61 259	3	1.	-16	< 172	- 572 - 74	9	1 -11 869 816	
16	0	6	1328 420	-1336 448	4 6 8	0	-16 -16	242 794 782	720	3 5	1	-17	263 4174	- 270 4560	9	1 -13 852 898 1 -14 242 - 223	
2		- 6 - 6	1938 629	1909	10 12	0	-16 -16	740	691 - 724	5	į	2	1766 331	-1858 236	9	1 -15 621 - 644	
6 8	ō	- 6 - 6	2828 846	-272Z - 797	14	0	-16 -16	< 197 565	137 592	5	i	4	794 1098	- 851 -1234	9	1 -17 < 163 167	
10	.0	- 6	2000	1858 1146	18	0	-16	< 182	- 25	5	i	6 7	240 476	- 258 - 472	11	1 1 321 360 1 2 < 211 - 143	
14	0	- 6 - 6	470 1649	- 445 -1595	10	0	-18 -18	747 240	- 984 - 321	5	ļ	8	476 720	509 - 721	!!	1 3 776 749 1 4 < 228 - 205 1 5 691 - 617	
18 20	ō	- 6 - 6	< 252 < 242	- 43	12	0	-18	256	313 - 459	5		10	451 240	- 416 216 - 678	11	1 6 < 236 - 150 1 7 1071 1110	
22 24	0	- 6	490 378	- 528 377	1 3 5	1	0	41,2 263 999	- 459 - 321 1089	5 5		12 13	649 616 < 143	- 678 - 625 - 151	11	8 < 221 - 154 1 9 1082 1084	
2	0	8 B	1524 711		7 9	i	Ö	879 1293	- 987 1334	5		- 1	2697		ii ii	1 10 < 172 - 117	

h	k 1	Fo	Fc	h	k	1	Fo	F_c	h	k	1	Fo	Fc	h	ĸ	1	Fo	Fc
11	1 - 1	546	462	. 12		-16	< 153	6	2	2	- 2	4433	-4594	8	2	- 4-	757	- 683
11	1 - 2	< 18Z	50						2	2	- 3	1347	1311	8	2	- 4 ⁻	1212	-1180
11	1 - 3	314 350	238	19	- !	1	1065	-1103	2	2	- 4 - 5	314 972	- 282 - 943	9	2 2	- 6 - 7	< 89	- 71
ii	1 - 5	2590	- 282 -2643	19 19		2	368 261	323 316	2	z	- 6	1593	-1611	8	2	- 8	1274	-1266 2172
11	1 - 6	900	- 789	19	i	4	< 137	- 22	2	2	- 7	< 89	- 74	8	2	- 9	< 108	8
!!	1 - 7	953 676	79 7 555	19		- 1	850	829	2	2	- 8 - 9	< 101 1014	1001	8 8	2	-10	203 590	- 247 660
ii	1 - 9	488	- 465	19	- i	- 2	881	- 829 - 865	ž	2	-10	1092	~1208	8	2	-12	486	514
11	1 -10	407	352	19	i	- 3	319	- 270	2	2	-11	306	290	8	2	-13	< 120	62
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ii	1 -13	< 236	- 145	19	i	- 6	< 232	- 191	2	2 2	-14	310	308	8	2	-16	157	- 148
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- 11	1 -15	< 215 < 192	- 130 - 45	19	1	- 8 - 9	< 230 954	229 - 965	2	2	-16	< 72	60	10	2		455	446
11	1 -17	197	- 193	19	i	-10	< 223	- 249	4	2	1	240	i 94	10	2	2	532	525
13	1 1	761	716	19	- !	~11 -12	< 217 < 207	224	4	2	2	1202	-1164 415	10	2	3	209 538	195 536
i s	i ż	397	- 379	19	- i	-12	1005	- 126 1085	4	2	4	573	541	10	ž	5	207	- 536 - 200
13	1 3	753	739	19	1	-14	< 176	114	4	2	5	507	- 443	10	2	6	1092	-1090
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13	1 -11	310 441	- 203 425	21	- 1	-14	< 141	- 21	4	2	- 9 -10	352 1212	- 311	10	2	-13 -14	23Z 683	- 273 699
13	1 -13	788	- 817	23		- 2	< 130	- 40	4	Z	-11	772	748	10	2	-15	105	164
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15	1 3	< 232	- 134 - 162	23 23	1	-10	< 155 < 145	- 62	6	2	2	794 1175	771 -1196	12	2 2	5	800 840	753 850
15	1 4	< 227 < 213	- 67	23		-11	< 145	- /	6	2	4	1913	1938	12	ž	6	534	528
15	1 6	453 < 170	- 430	0	2	1	1615	1557	6	z	5	1344	-1429	12	Z	8	190	178
15	1 7	< 134	- 172 117	0	2	2	1239 879	1304	6	2	6	221	-1078 - 232	12	2	9	215	225
				ō	2	4	122	81	6	2	8	215	~ 228	12	2	- 1	1129	1148
15	1 - 1	< 227	- 116	o o	2	5	2143	103 -2094	6	z	10	1200	- 175	12	2	- 2 - 3	2370	-2410 273
15	1 - 3	397	- 314	ິ້ນ	2	6 7	265	245	6	2	1.1	1007	- 869	iz	z	- 4	234 271	280
15	1 - 4	865	- 824	J	2	8	794	743	6	2	12	95 530	- 108	12	2	- 5	1144	-1139
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15	1 - 7	672	649	0	2	- 11	978	1040	6	2	- 1	215	207	12	2	- 8 - 9	569	- 554
15	1 - 8	1206 < 232	1197 97	o o	2	12	484	471	6	Z	- ż	540 499	- 530 - 458	12	2	- 9 -10	227 < 157	- 233 - 77
15	01-1	263	273	ō	2	14	< 112 194	- 83 186	6	2	- 4	873	771	12 12	2	-11	< 120	99
15 15	1 -11	472 < 234	429 - 81	٥	2	15	122	- 129	6	z	- 5 - 6	182 4170	- 68 4232	12	2	-12 -13	64 I 75 I	- 665
15	1 -13	< 227	83	2	2	0	130	- 49	6	2	- 7	2240	2235	12	z	-14	751 594	- 748 586
15	1 -14	< 215 755	52 814	4	2	0	2631	2886	6	2	- 8	606	554 1150	12	2	-15	186	- 163
15	1 -16	755 498	814 463	6 8	2	0	2046 486	2077 - 484	6	Z	-10	862	- 854	12	2	-16 -17	459 110	435 127
15	1 -17	352	- 368	10	2	0	1903	-1983	6	2	-11	228	186					
17		817	- 601	12	2	0	294	254	6	2	-12 -13	813 147	823 184	14	2	1 2	465	453
17	1 2	310	- 8CI - 318	14 16	2	0	538 < 145	479 ~ 17	6	2	-14	114	- 116	14	2	3	1355	-1441 1090
17		1156	-1122	18	2	0	420	351	6	2	-15	544	484	14	2	4	478	445
17	1 4	28,t 318	200 316	20	2	0	449	~ 415	6	2	-16 -17	130 223	161 269	14	2 2	5	205 819	198 784
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17	1 - 1	1243	1304	2	2	2	1946	2016 - 359	8 8	2	1 2	610 860	- 619 - 843	14	2	8	166	- 168
17	1 - 2	652	- 662	2 2	2	4	1708	- 1694	8	Z	3	786	- 808	14	z	- 1	184	- 189
17	1 - 3	426	- 369	2	2	5	2195	2240	8	2	4	368	320	14	2	- 2 - 3	< 116	- 50
17	1 - 4	< 236 < 236	70 - 163	2 2	2 2 2 2 2 2 2	6 7	534 1839	- 491 1844	8	-2	6	159 966	- 939	14	2	- 4	1140	1194
17	1 - 6	680	- 656	2 2	2	8	1651	1594	ě	2	7	159	- 181	14	2	- 5	1471	- 527 1573
17	1 - 7	865 908	868 - 938	2 2	2	10	465 < 120	472 137	8	2 2 2 2	8	< 120 492	- 504	14	2	- 6 - 7	976	-1038 939
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17	1 -13	234	- 248	2	z	15	451	445	8	2	- 1	432	- 359	14	2	-12	< 118	÷ 50
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22 22	2 2	-11 -12	√ 66	- 188 - 46	5 5 5	3	-10 -11 -12	269 < 238 285	- 229 - 20 269	13	3	6 7	563 426	- 393	8 10 12	4	0	347 354 240	345 438 ~ 268
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į	3	3	1028 275	-1137 240	7	3	11	< 182 219	- 189 - 176	13	3	-14 -15	633 308	- 627 - 283	2 4 6	6 6	0	294 271 < 110	- 209 206 - 66
	3 3	5 6 7	< 161 1382 925	- 43 -1513 - 997	7 7	3	- I - Z	1512 207	-1511 149	15 15	3	! 2	755 1036	- 674 1049	8	6	0	438 335	- 431 275

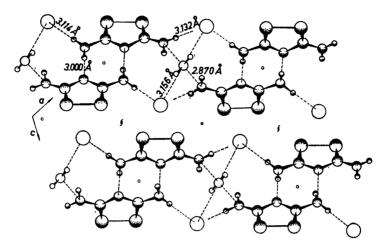


Fig. 6. The arrangement of ions in the unit cell as seen along the b-axis. Broken lines indicate hydrogen bonds.

exocyclic nitrogen atoms of a thiuret ion form hydrogen bonds N-H...Cl, 3.114 and 3.132 ± 0.007 Å long, to the chloride ions of the linear Cl···S-S···Cl arrangement. There are two $O-H\cdots Cl$ hydrogen bonds, of length 3.156+0.006Å, and two N-H...O hydrogen bonds, of length 2.870 \pm 0.010 Å. This gives the water oxygen approximately tetrahedral surroundings.

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