

## The Crystal and Molecular Structure of Thiuret Hydrochloride Hemihydrate

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The crystal and molecular structure of the unsaturated five-membered 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  $1.342 \pm 0.010$  Å and  $1.350 \pm 0.009$  Å, and the lengths of the exocyclic C-N bonds are  $1.315 \pm 0.009$  Å and  $1.303 \pm 0.010$  Å. The C-S bond lengths are  $1.767$  and  $1.762 \pm 0.007$  Å, and the S-S bond length is  $2.071 \pm 0.004$  Å.

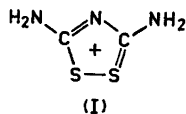
The thiuret ion is essentially planar, and nearly symmetric about an axis through the cyclic nitrogen atom and the midpoint of the sulphur-sulphur bond. The bond lengths show that the ion is stabilized through  $\pi$ -orbital delocalization, the conjugation being most pronounced in the carbon-nitrogen 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 hydroiodide and hydrobromide is also present in crystals of thiuret hydrochloride hemihydrate. In the latter compound the chlorine-sulphur distances in this arrangement, are  $3.864 \pm 0.004$  Å and  $3.527 \pm 0.004$  Å, and the interaction between halogen and sulphur is weaker than in thiuret hydroiodide and hydrobromide.

The following hydrogen bonds occur in the crystal,  
 $N-H\cdots O = 2.870 \pm 0.010$  Å     $N-H\cdots N = 3.000 \pm 0.010$  Å,  
 $N-H\cdots Cl = 3.114$  and  $3.132 \pm 0.007$  Å, and  $O-H\cdots Cl = 3.156 \pm 0.006$  Å.

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



of the valences of the two sulphur atoms,<sup>1</sup> it has been found to be planar in unsaturated five-membered cyclic disulphides.<sup>2-8</sup> Foss<sup>2</sup> has suggested that the stability of the planar disulphide group in these compounds is due to  $\pi$ -bonding in which  $\pi$ -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.<sup>2-8</sup> 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  $\pi$ -bonding with ring atoms. In mono-phenyl substituted 1,2-dithiolium ions, for example,<sup>6,9</sup> 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,<sup>10</sup> 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.<sup>4,5</sup> In the latter compounds the cyclic carbon atoms, bonded to the disulphide group, strongly engage in  $\pi$ -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  $\pi$ -bonding with an external atom.<sup>3</sup> 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  $1.747 \pm 0.017$  Å and the length of the C–S bond on the other side of the ring is  $1.713 \pm 0.017$  Å. Furthermore, the length of the sulphur-sulphur bond is reported to be  $2.047 \pm 0.007$  Å, and Jeffrey and Shiono<sup>3</sup> 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<sup>10</sup> has calculated the  $\pi$ -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 hydroiodide<sup>2</sup> and hydrobromide,<sup>8</sup> 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  $\sigma$ -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.<sup>11</sup> The crystals are monoclinic, with the unit cell dimensions (redetermined):  $a = 19.53 \text{ \AA}$ ,  $b = 5.47 \text{ \AA}$ ,  $c = 14.31 \text{ \AA}$ , 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  $\text{CuK}\alpha$  radiation. A crystal with cross-section  $0.16 \times 0.27 \text{ mm}$  was used for the recordings around the *b* axis; for the  $hk0$ -recordings a crystal with cross-section  $0.3 \times 0.08 \text{ mm}$  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.<sup>12</sup> A more detailed description of the procedure is given here.

Observed  $h0l$  structure factors were put on an absolute scale by means of Wilson's method,<sup>13</sup> 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  $14,0,\bar{1}4$  were chosen positive, and combination of these two reflections in a Harker Kasper inequality gave the sign for  $18,0,\bar{8}$ . The signs for  $12,0,4$ ,  $10,0,0$ ,  $12,0,2$ , and  $12,0,\bar{1}2$  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  $10,0,0$ ,  $80\bar{8}$  and  $12,0,\bar{1}2$  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 the direct structure determination.

$h$	$l$	$100u$	sign	$h$	$l$	$100u$	sign
0	16	42	$ad$	2	8	37	$bc$
10	0	90	$b, dc$	4	-8	63	$a$
16	0	42	$abd$	8	-8	78	$b, c$
2	2	36	$ab$	14	-8	51	$abd$
8	-2	65	$a$	18	-8	84	$+$
12	-2	68	$c$	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	$c$
12	4	106	$a$	6	-12	40	$a$
16	4	49	$c$	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	$b$	14	-14	78	$+$
6	-6	43	$b, c$	20	-14	76	$ad$
10	-6	38	$abc$	10	-16	36	$abd$
16	-6	50	$d$				

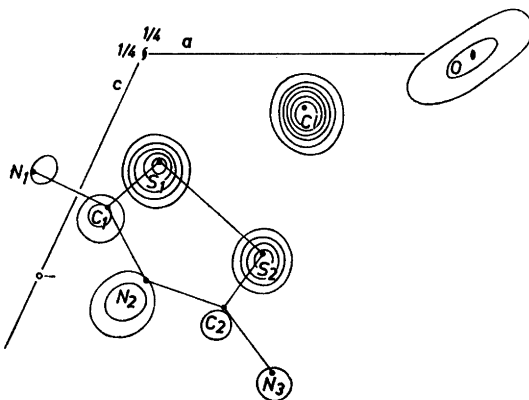


Fig. 1. Fourier map of thiuret hydrochloride hemihydrate in the  $b$ -axis projection, based on the 37 reflections in Table 1. with  $a = +$ ,  $b = c = -$  and  $d = +$ . Contours at arbitrary but equal intervals.

*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  $N-H\cdots N$  hydrogen bonds of length about 3.0 Å. Such an arrangement of thiuret ions was found in thiuret hydrobromide,<sup>8</sup> the  $N-H\cdots N$  distance there being 3.07 Å. Furthermore, an approximately linear  $Cl\cdots S-S\cdots Cl$  arrangement was assumed, from the  $X\cdots S-S\cdots X$  arrangements found in thiuret hydroiodide and hydrobromide.<sup>2,8</sup> 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<sup>II</sup> computer, using a program designed by Mair.<sup>14</sup> Weighting scheme No. 3, recommended by Mair, was used with  $a = 12$  and  $b = 7.5$ . The refinement comprises the  $h0l$ ,  $h1l$ ,  $h2l$ ,  $h3l$ , 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  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  is 0.059. Eight low order reflections, supposed to

Table 2. Final atomic coordinates from the least squares refinement.

Atom	$x$	$y$	$z$
Cl	0.11067	0.25841	0.18718
S <sub>1</sub>	0.20221	0.81731	0.12798
S <sub>2</sub>	0.09096	0.81664	0.02381
N <sub>1</sub>	0.2923	0.4716	0.1136
N <sub>2</sub>	0.1697	0.4463	-0.0077
N <sub>3</sub>	0.0426	0.4605	-0.1121
C <sub>1</sub>	0.2232	0.5545	0.0736
C <sub>2</sub>	0.1016	0.5517	-0.0383
O	0.0000	-0.0513	0.2500
H <sub>1</sub>	0.299	0.336	0.093
H <sub>2</sub>	0.323	0.530	0.178
H <sub>3</sub>	0.047	0.358	-0.147
H <sub>4</sub>	-0.003	0.521	-0.133
H <sub>5</sub>	-0.030	0.047	0.250

Table 3. Components of atomic vibration tensors  $U^r$  in  $\text{\AA}^2$ , referred to crystallographic axes.

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{23}$	$U_{31}$
Cl	0.0348	0.0632	0.0453	0.0133	0.0128	0.0178
S <sub>1</sub>	0.0348	0.0509	0.0376	0.0023	-0.0084	0.0148
S <sub>2</sub>	0.0333	0.0525	0.0433	0.0085	-0.0017	0.0161
N <sub>1</sub>	0.0330	0.0595	0.0397	0.0069	-0.0131	0.0071
N <sub>2</sub>	0.0296	0.0446	0.0350	0.0043	-0.0011	0.0128
N <sub>3</sub>	0.0271	0.0648	0.0439	0.0058	-0.0041	0.0069
C <sub>1</sub>	0.0292	0.0619	0.0297	0.0008	0.0014	0.0153
C <sub>2</sub>	0.0292	0.0532	0.0338	0.0029	0.0012	0.0134
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<sub>1</sub>...H<sub>5</sub>, are -0.1, 0.7, 1.9, 1.7, and 1.8  $\text{\AA}^2$ , 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  $F_o = F_c$ .

Atomic coordinates and components of atomic vibration tensors  $U^r$  are given in Tables 2 and 3. The observed and calculated structure factors are

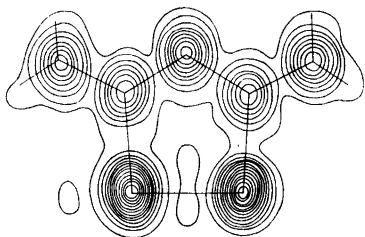


Fig. 2. Electron density map of the thiuret ion, showing the electron density in the plane of the ion. Contour intervals for carbon and nitrogen  $1 \text{ e.}\text{\AA}^{-3}$  and for sulphur  $2 \text{ e.}\text{\AA}^{-3}$ . Lowest contour at  $1 \text{ e.}\text{\AA}^{-3}$ .

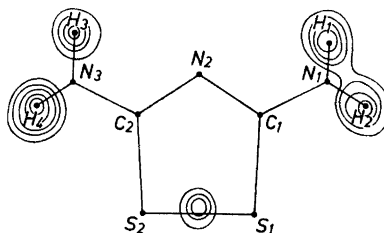


Fig. 3. Electron density map in the plane of the thiuret ion with all atoms but the hydrogens subtracted. Contour intervals of  $0.1 \text{ e.}\text{\AA}^{-3}$  starting at  $0.3 \text{ e.}\text{\AA}^{-3}$ .

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<sup>15</sup> 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<sup>16</sup> 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<sup>11</sup>.

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,<sup>16</sup> 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.<sup>17</sup> 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.

	$a$	$b$	$c$
$L$	-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.

Atom	(a)			(b)		
	$L$ (Å)	$M$ (Å)	$N$ (Å)	$L$ (Å)	$M$ (Å)	$N$ (Å)
$S_1$	-1.031	0.970	0.016	-1.035	0.975	0.016
$S_2$	1.031	0.964	-0.017	1.035	0.969	-0.017
$N_1$	-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
$C_1$	-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  $V^i$  in Å<sup>2</sup> as found by the least squares refinement (exp) and as calculated from the rigid-body parameters (RB).

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

Table 7. Final rigid-body translation parameters  $T_{ij}$  and libration parameters  $\omega_{ij}$ .

	<i>LL</i>	<i>MM</i>	<i>NN</i>	<i>LM</i>	<i>MN</i>	<i>LN</i>
$T$ (Å)	0.03036	0.03908	0.03250	-0.00364	-0.00922	0.00032
$\omega$ (rad <sup>2</sup> )	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.

	<i>L</i>	<i>M</i>	<i>N</i>
$T_1^2 = 0.0462 \text{ \AA}^2$	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
$\omega_1^2 = 0.0060 \text{ rad}^2$	-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)	$\sigma(l)$ (Å)
$S_1-S_2$	2.071 (2.063)	0.004
$S_1-C_1$	1.767 (1.761)	0.007
$S_2-C_2$	1.762 (1.756)	0.007
$C_1-N_2$	1.342 (1.337)	0.010
$C_2-N_2$	1.350 (1.345)	0.009
$C_1-N_1$	1.315 (1.310)	0.009
$C_2-N_3$	1.303 (1.298)	0.010
$N_1-H_1$	0.83	0.1
$N_1-H_2$	0.93	0.1
$N_3-H_3$	0.77	0.1
$N_3-H_4$	0.89	0.1



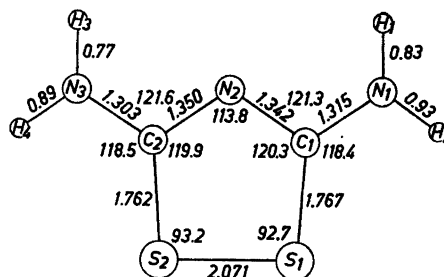


Fig. 4. Bond lengths (Å) and bond angles (°) in the thiuret ion.

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

	Angle (°)	$\sigma$ (°)
$C_1-S_1-S_2$	92.7 ( 92.7)	0.3
$S_1-C_1-N_1$	120.3 (120.3)	0.5
$S_1-C_1-N_2$	118.4 (118.4)	0.6
$N_1-C_1-N_2$	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
$N_2-C_2-N_3$	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.<sup>8</sup> For thiuret hydroiodide a non-planar disulphide ring is indicated<sup>2</sup> 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<sub>2</sub> 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.<sup>22</sup> In the unsaturated five-membered cyclic disulphide xanthan hydride,<sup>4</sup> 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,<sup>18</sup> where the C—S bonds are found to be 1.83 and  $1.85 \pm 0.02$  Å. Even if the carbon atoms bonded to sulphur in the latter compound are mainly *sp*<sup>3</sup>-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,<sup>19</sup> a C—S bond of 1.76 Å corresponds to a  $\pi$ -bond order of about 0.4.

The length of the sulphur-sulphur bond in thiuret hydrochloride hemihydrate is found to be  $2.071 \pm 0.004$  Å. This value includes correction for rigid-body libration; the uncorrected value is 2.063 Å. In thiuret hydrobromide<sup>8</sup> and hydroiodide,<sup>2</sup> where corrections for rigid-body libration were not undertaken, the sulphur-sulphur bond lengths are  $2.081 \pm 0.009$  and  $2.088 \pm 0.012$  Å, respectively. A least squares refinement of the thiuret hydroiodide structure<sup>7</sup> gave for the sulphur-sulphur bond a length of  $2.083 \pm 0.015$  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,  $2.071 \pm 0.004$  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.<sup>20</sup> 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,<sup>21</sup> 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  $\sigma$ -bond order about 0.10, is probably too weak to affect the sulphur-sulphur bond length. In thiuret hydrobromide and hydro-

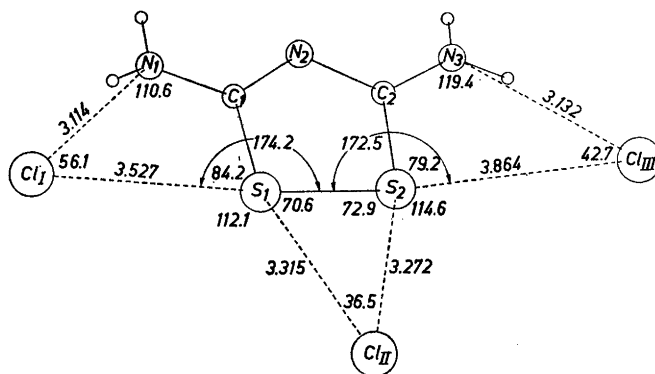


Fig. 5. Atomic distances and angles with reference to the environment of the disulphide group.

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)	$\sigma$ (Å)
S <sub>1</sub> ...Cl <sub>I</sub>	3.527	0.004
S <sub>1</sub> ...Cl <sub>II</sub>	3.315	0.004
S <sub>2</sub> ...Cl <sub>II</sub>	3.272	0.004
S <sub>2</sub> ...Cl <sub>III</sub>	3.864	0.004
N <sub>1</sub> ...Cl <sub>I</sub>	3.114	0.007
N <sub>3</sub> ...Cl <sub>III</sub>	3.132	0.007
	Angle (°)	$\sigma$ (°)
Cl <sub>I</sub> ...N <sub>1</sub> -C <sub>1</sub>	110.6	0.5
Cl <sub>I</sub> ...S <sub>1</sub> -C <sub>1</sub>	84.2	0.3
Cl <sub>I</sub> ...S <sub>1</sub> -S <sub>2</sub>	174.2	0.2
Cl <sub>I</sub> ...S <sub>1</sub> ...Cl <sub>II</sub>	112.1	0.2
S <sub>1</sub> ...Cl <sub>I</sub> ...N <sub>1</sub>	56.1	0.3
Cl <sub>II</sub> ...S <sub>1</sub> -S <sub>2</sub>	70.6	0.3
Cl <sub>II</sub> ...S <sub>2</sub> -S <sub>1</sub>	72.9	0.3
Cl <sub>II</sub> ...S <sub>2</sub> ...Cl <sub>III</sub>	114.6	0.2
S <sub>1</sub> ...Cl <sub>II</sub> ...S <sub>2</sub>	36.5	0.2
Cl <sub>III</sub> ...S <sub>2</sub> -S <sub>1</sub>	172.5	0.2
Cl <sub>III</sub> ...S <sub>2</sub> -C <sub>2</sub>	79.2	0.3
Cl <sub>III</sub> ...N <sub>3</sub> -C <sub>2</sub>	119.4	0.5
S <sub>2</sub> ...Cl <sub>III</sub> ...N <sub>3</sub>	42.7	0.3

iodide 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  $\sigma$ -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 hemihydrate. 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  $\sigma$ -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...N hydrogen bonds of length 3.000 ± 0.010 Å. The



Table with multiple columns labeled h, k, l, P\_o, P\_c, representing crystallographic data points across various indices.



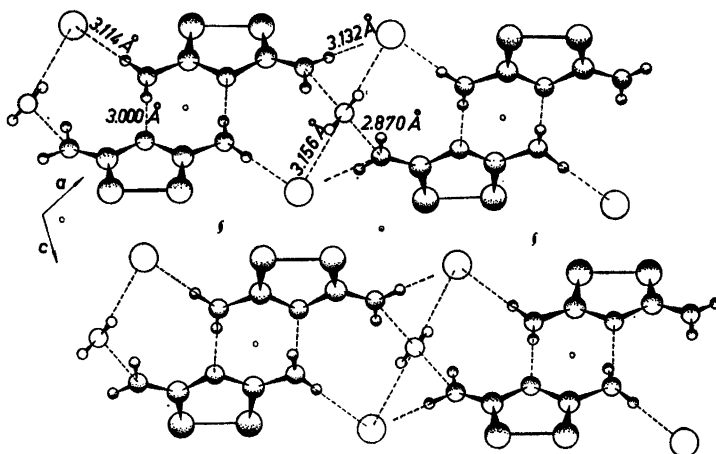


Fig. 6. The arrangement of ions in the unit cell as seen along the  $b$ -axis. Broken lines indicate hydrogen bonds.

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

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