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The Constitution of the Formamidinium Disulphide Ion, from the Crystal Structures of the Diiodide and Dibromide

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The unit cells of formamidinium disulphide diiodide (I) and dibromide (II) monohydrates, $[(H_2N)_2C-S-S-C(NH_2)_2]X_2 \cdot H_2O$, are: I, $a = 5.15$ Å, $b = 16.52$ Å, $c = 13.39$ Å; space group, D_{2h}^{10}-$Pccn$ with $Z = 4$. II, $a = 8.61$ Å, $b = 5.12$ Å, $c = 12.40$ Å, $\beta = 99\frac{1}{2}°$; space group, $C_{2h}^{4}-P2/c$ with $Z = 2$. The structures have been determined by two-dimensional X-ray methods.

The crystals are built up of formamidinium disulphide cations and halide anions, and water of crystallization; the cation possesses, by space group requirements, a twofold axis of symmetry in both salts. The disulphide group has normal configuration and dimensions, with $S-S = 2.04$ Å, and $\angle S-S-C = 99°$ and $104°$, CSS/SSC dihedral angle $= 105°$ and $89°$, in I and II, respectively. The dimensions of the thiourea groups are as in the thiourea molecule before oxidation to formamidinium disulphide cation, but for a slight lengthening of the C—S bond. There is a small but not significant deviation from planarity of the thiourea groups, and no significant difference between the lengths of the two C—N bonds of a group. In both salts the water molecules lie on twofold axes, and each participates in hydrogen bonds with two halide ions and two nitrogen atoms.

Salts of formamidinium disulphide are formed from thiourea by the action of oxidizing agents such as chlorine[1], bromine[1–5], iodine[6–13], cupric ion[14,15], hydrogen peroxide[7,11,15,16], peroxydisulphate ion[8], peroxyacetic acid[15], sulphonyl chlorides[6], sulphuryl chloride[10], permanganate[7], and by anodic oxidation[17,18]:

$$2\ (H_2N)_2CS = [(H_2N)_2C—S—S—C(NH_2)_2]^{++} + 2\ e \qquad (1)$$

Conversely, the disulphide may be reduced to thiourea by means of sodium amalgam[1], hydrogen sulphide[2], nascent hydrogen[10], or cathodically[18]. The reaction of thiourea with iodine:

$$2\ (H_2N)_2CS + I_3^- = [(H_2N)_2C—S—S—C(NH_2)_2]^{++} + 3\ I^- \qquad (2)$$

leads to an equilibrium which can be readily approached from either side [6–13]. Thus, in dilute solutions thiourea may be titrated quantitatively with iodine [9], whereas on dissolving crystals of formamidinium disulphide diiodide in water [6,8,10], on addition of potassium iodide to a solution of the dichloride or other salts [6,8,10], or on addition of solvents of low ionizing power such as methanol, ethanol or acetone to an aqueous solution of the diiodide [8,10,13], iodine is liberated. From potentiometric measurements, Preisler and Berger [16] found the oxidation-reduction potential of the reversible thiourea-formamidinium disulphide system (1) to be 0.42 V at 30°C, referred to the normal hydrogen electrode, for solutions at constant ionic strength containing 0.05 N to 1 N hydrochloric acid. The results of Preisler and Berger have later been confirmed by Freedman and Corwin [19]. Together with the potential, 0.54 V, of the iodide-triiodide system, this gives $K = 10^4$ for the equilibrium constant of reaction (2), in close agreement with the value obtained by Mahr [12] from spectrophotometric measurements of iodine concentration in equilibrium mixtures.

A number of salts of formamidinium disulphide have been isolated and characterized. The sparingly soluble dinitrate [5–8,10,11,17] separates on addition of nitric acid or nitrates to solutions of other salts, or on oxidation of thiourea in presence of nitrate ions.

The salts show normal disulphide reactivity. Typical heterolytic cleavage of the S–S bond takes place in the reaction with cysteine (RSH) to produce [11] in the first step a mixed disulphide:

$$[(H_2N)_2C-S-S-C(NH_2)_2]^{++} + RS^- = [RS-S-C(NH_2)_2]^+ + (H_2N)_2CS \qquad (3)$$

and in the second step cystine:

$$[RS-S-C(NH_2)_2]^+ + RS^- = RS-SR + (H_2N)_2CS \qquad (4)$$

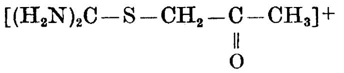
The hydrolysis of the disulphide [1,6], to give thiourea, sulphur and cyanamide, has been formulated thus [11]:

$$[(H_2N)_2C-S-S-C(NH_2)_2]^{++} + OH^- = [(H_2N)_2C-S-OH]^+ + (H_2N)_2CS \qquad (5)$$

with subsequent decomposition of the sulphenyl hydroxide, although it appears that an alternative mechanism involving a nucleophilic attack on carbon instead of sulphur cannot be excluded. Likewise, the reaction with cyanide ion [2], which leads to the same products as the hydrolysis reaction except for the formation of thiocyanate ion instead of sulphur, may be interpreted in terms of a nucleophilic attack of cyanide ion on sulphur, to give the species

$$[(H_2N)_2C-SCN]^+$$

as an intermediate. Heterolytic fission of the disulphide link has been considered [20] as a possible first step in the reaction of the disulphide with secondary and primary amines. The reaction of the disulphide with acetone and other ketones to give substituted 2-aminothiazoles [4] is likely to involve a first step analogous to halogenation reactions of ketones, to produce



$$[(H_2N)_2C-S-CH_2-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3]^+$$

with subsequent ring closure under elimination of water.

The tetramethyl analogue of formamidinium disulphide has been isolated as the perchlorate by Lecher *et al.*[21], from the reaction of tetramethylthiourea with bromine. Sahasrabudhey [22,23] prepared also the chloride and bromide, and demonstrated the reactions:

$$[(Me_2N)_2C-S-S-C(NMe_2)_2]^{++} + 2\ S_2O_3^{--} = (S_2O_3)_2^{--} + 2\ (Me_2N)_2CS \qquad (6)$$

$$[(Me_2N)_2C-S-S-C(NMe_2)_2]^{++} + 2\ (H_2N)_2CS = \\ = [(H_2N)_2C-S-S-C(NH_2)_2]^{++} + 2\ (Me_2N)_2CS \qquad (7)$$

Eqn. (7) represents a readily displaceable equilibrium. Although quite different explanations are implicit in Sahasrabudhey's arguments, reactions (6) and (7) have the appearance of typical two-step nucleophilic displacements, involving heterolysis of the S—S bond of the original disulphide in the first step, and of the S—S bond of a mixed disulphide in the second step, like the two steps of the formamidinium disulphide-cysteine reaction given by Eqs. (3) and (4) above.

The disulphide nature of the salts is well established, and has indeed not been questioned until Sahasrabudhey [5,13,22,23] in 1951—53 argued that they were not disulphides, but monomeric compounds derived from a single thiourea molecule. His experimental results, of which some are referred to above, are in fact in complete accord with the disulphide formula, but were by Sahasrabudhey construed to imply a "rather unusual type of link" [23] between the oxidized thiourea residue and the anion, something like "a free radical, Weitz's or Wurster's salt" structure. His cryscopic measurements in glacial acetic acid [22,23] gave values of 190—220 for the molecular weight of the tetramethyl derivative of the dibromide, as compared with 212 required for the monomeric formula Me_2NCSBr; however, the results agree equally well with the double formula for a salt composed of three ions.

The present X-ray crystallographic work serves to establish the disulphide nature of the salts in the crystalline state. There should be no reason to suspect that the disulphide bond is not preserved in solution, insofar as cleavage through ordinary chemical interactions does not take place.

CRYSTAL DATA

Unit cell and space group data were derived from oscillation and Weissenberg photographs of single-crystal specimens. The axial lengths are based on $\lambda(\mathrm{Cu}K\alpha) = 1.542$ Å and are probably accurate to within 0.5 %. Densities were determined by flotation in mixtures of carbon tetrachloride with benzene or bromoform.

Formamidinium disulphide dichloride, $[(H_2N)_2CS]_2Cl_2$. Orthorhombic bipyramidal, $a = 10.54$ Å, $b = 19.75$ Å, $c = 8.85$ Å. There are eight formula units per unit cell; density, calc. 1.61, found 1.57 g/cm^3. The space group, from systematic absences, is $D_{2h}^{15} — Pbca$. The crystals occurred as long prisms {021}.

Formamidinium disulphide dibromide monohydrate, $[(H_2N)_2CS]_2Br_2 \cdot H_2O$. Monoclinic, $a = 8.61$ Å, $b = 5.12$ Å, $c = 12.40$ Å, $\beta = 99\frac{1}{2}°$. Two formula units per unit cell; density, calc. 2.04, found 2.04 g/cm^3. Systematic absences, $h0l$ when l is odd. These are characteristic of the space groups, $C_{2h}^{4} — P2/c$ and $C_s^{2} — P/c$, of which the former would require that the formamidinium disulphide ion possess a centre or a twofold axis of symmetry.

The crystals were obtained as plates {100}, or as flat prisms bounded by {100} and, less developed, {001}.

Formamidinium disulphide diiodide monohydrate, $[(H_2N)_2CS]_2I_2 \cdot H_2O$. Orthorhombic bipyramidal, $a = 5.15$ Å, $b = 16.52$ Å, $c = 13.39$ Å. Four formula units per unit cell; density, calc. 2.47, found 2.47 g/cm^3. The space group, from systematic absences, is $D_{2h}^{10} — Pccn$, which has eightfold general positions, and centres of symmetry and twofold axes as special, fourfold positions.

The crystals were well developed prisms, elongated along the *a* axis and in most cases flattened along the *c* axis.

The diiodide (I) and later the dibromide (II) were chosen for further study. The results on II indicate that the centrosymmetric space group, $C_{2h}^4 - P2/c$, is the correct one. Twofold symmetry of the disulphide ion is thereby crystallographically required in both salts; of the two possibilities the molecular symmetry element was found to be a twofold axis and not a symmetry centre. The latter would have led to a planar, *trans* disulphide group; the only planar disulphide group yet found is the *cis* group occurring in thiuret hydroiodide [24].

A preliminary account of the structure of the diiodide has been published [25].

EXPERIMENTAL

The dichloride was prepared from thiourea in hydrochloric acid solution by oxidation with hydrogen peroxide as described by Preisler and Berger [16], the dibromide by slowly adding the equivalent amount of bromine to a 20 % aqueous solution of thiourea, under cooling in ice water, and the diiodide as described by Marshall [8], by gradually adding 5 parts of iodine crystals to 3 parts of powdered thiourea in 25 parts of water, and subsequent cooling.

The measured densities as compared with the X-ray densities, and the occurrence of peaks of reasonable height on the twofold axes in the electron density maps, leave no doubt that the crystals of I and II are monohydrates, although no mentioning of water of crystallization in these salts is found in literature. However, the analyses by McGowan [6] and Werner [10] of I and by Hunter and Jones [3] of II agree better with monohydrates than anhydrous salts. Boeseken [15] obtained the dichloride as a pentahydrate, whereas the present crystals, and preparations analyzed by earlier workers [6,18], were anhydrous.

For the structure determinations, the intensities of the $0kl$ and $hk0$ reflections of I and the $h0l$ and $0kl$ reflections of II were estimated visually from zero-layer Weissenberg photographs. Copper radiation was used, and crystals with cross-sections of 0.04 × 0.05 mm and 0.07 × 0.05 mm, respectively, for the *a*- and *c*-axis photographs of I, and 0.11 × 0.09 mm and about 0.1 × 0.1 mm, respectively, for the *b*- and *a*-axis photographs of II. The absorption coefficient for Cu*Ka* radiation is 499 and 130 cm^{-1} for I and II, respectively. No corrections for absorption were made, and absorption effects are undoubtedly reflected in the temperature corrections later applied to the calculated structure factors. In the case of I, 98 out of 144 $0kl$ reflections and 48 out of 60 $hk0$ reflections within the range $\sin \Theta < 0.985$ were recorded with measurable intensity, the corresponding figures for II being 124 out of 130 $h0l$ reflections and 71 out of 81 $0kl$ reflections. They were converted to relative structure amplitudes in the usual way, and eventually put to an approximately absolute scale by comparison with the calculated values.

Viervoll and Ögrim's [26] atomic scattering curve for sulphur was used in the calculation of structure factors, and the curves of Berghuis *et al.*[27] for oxygen, nitrogen and carbon. The hydrogen contributions were ignored in both structures. For the iodide and bromide ions, curves were constructed based on the Thomas-Fermi values for xenon and krypton, respectively, at small scattering angles and for electroneutral iodine and bromine at intermediate and larger scattering angles.

Summations were made by means of Beevers-Lipson strips, at 12° intervals along the *a* axis of I and the *a* and *b* axes of II, and at 6° intervals along the other axes.

THE STRUCTURE ANALYSES

The structures were solved by use of the heavy atom method, the positions of the iodide and bromide ions being found from Patterson projections. Although the vector maps gave also the position of the one sulphur atom of the asymmetric unit, the signs used in the first F_o synthesis were in each case

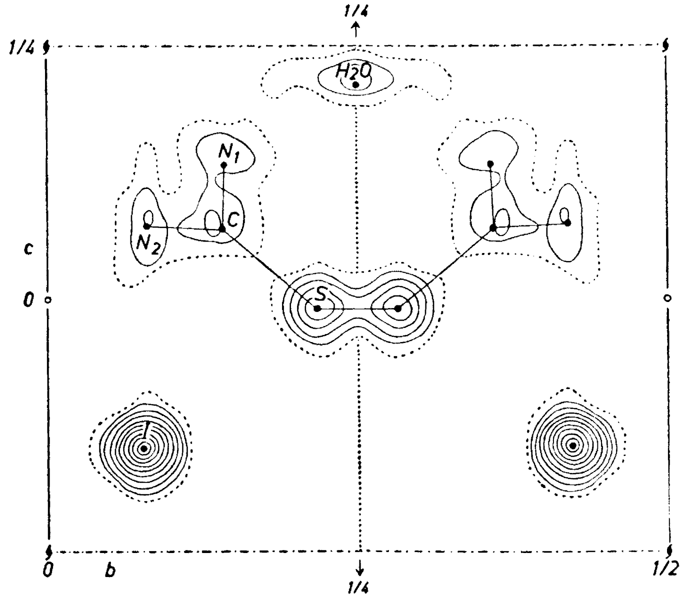


Fig. 1. Electron density projection of formamidinium disulphide diiodide monohydrate (I) along the *a* axis. The figure shows two asymmetric units. Contours at intervals of 10 e · Å^{-2} for the iodide ion, 5 e · Å^{-2} for sulphur, 4 e · Å^{-2} for oxygen and 3 e · Å^{-2} for the carbon and nitrogen atoms. The 3-electron line is dashed. The final atomic positions are marked with dots, and lines drawn to indicate the outline of the disulphide cation.

based on the contributions of the heavy atom alone, and the location of the sulphur peak appearing in the first electron density map was then checked against the coordinates derived from the vector map. In the projec-

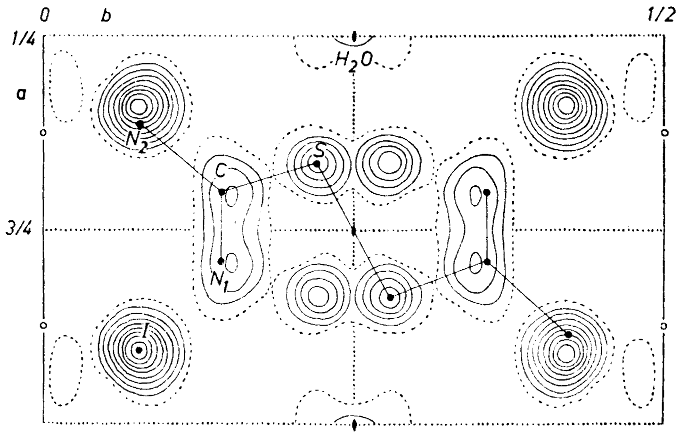


Fig. 2. Electron density projection of I along the *c* axis, showing four asymmetric units. The 6-electron line is dashed, and contours are at intervals of 10 e · Å^{-2} for the iodide ion and 5 e · Å^{-2} for the other atoms.

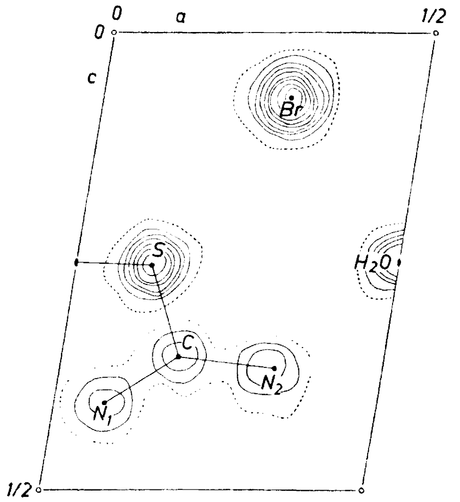


Fig. 3. Electron density projection of the asymmetric unit of formamidinium disulphide dibromide monohydrate (II) along the *b* axis. The 3-electron line is dashed, and contours are at intervals of 6 e · $Å^{-2}$ for the bromide ion, 3 e · $Å^{-2}$ for sulphur and oxygen and 2 e · $Å^{-2}$ for carbon and nitrogen. The final atomic positions are marked with dots, and the outline of one thiourea group is drawn; the other thiourea group (not shown) of the disulphide cation lies on the other side of the twofold axis.

tion along the short axis of each salt, the approximate positions of also the lighter atoms could be determined from the first electron density map, whereas in the projection along the second longest axis, overlapping occurred, of iodine and nitrogen and of carbon and nitrogen in the *c*-axis projection of I, and of carbon and nitrogen and of sulphur and oxygen in the *a*-axis projection of II. The y coordinates in the case of I, and z coordinates in the case of II, of the overlapped lighter atoms were at first put equal to those determined from the better resolved short-axis projections, and preliminary x and y coordinates, respectively, were assigned on the basis of assumed bond lengths and angles. When F_0 refinement had led to the determination of the sign of all but a few very weak reflections of a zone, further refinement was carried out by means of repeated $(F_0 - F_c)$ syntheses.

The two electron density projections of the diiodide are shown in Figs. 1 and 2, and those of the dibromide in Figs. 3 and 4. The atomic coordinates are given in Tables 1 and 2. In the case of II, Table 2, the coordinates used for the last structure-factor calculations were corrected on the basis of the gradients still present at some atomic positions in the last difference map for each zone. Two sets of z coordinates for II were obtained, one from each zone; where the corrected values differed the final value was taken as the mean of the two, weighted according to their apparent reliability. The two sets of y coordinates for I, used together with the x and z coordinates of Table 1 for the last structure-factor calculations, were: $y(\mathrm{I}) = 0.0782$ and 0.0785, $y(\mathrm{S}) = 0.2195$ and 0.2185, $y(\mathrm{C}) = 0.139$ and 0.144, $y(\mathrm{N_1}) = 0.140$ and 0.145, $y(\mathrm{N_2}) = 0.080$

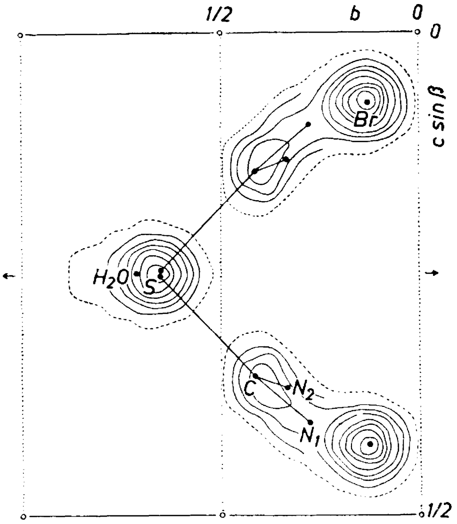


Fig. 4. Electron density projection of II along the *a* axis. One disulphide cation (two asymmetric units) is shown. The 6-electron line is dashed, and contours are at intervals of 6 e . $Å^{-2}$ for bromine, sulphur and oxygen, and 3 e . $Å^{-2}$ for carbon and nitrogen. The map shows that the final atomic positions (marked with dots) correspond to not quite planar thiourea groups, and that the best plane of a group is nearly parallel to the projection axis.

and 0.079, from the 0*kl* and *hk*0 data, respectively. The *y* values of Table 1 are in the case of C, N_1 and N_2 from the 0*kl* data; for I and S they are weighted means.

Table 1. Atomic coordinates for formamidinium disulphide diiodide monohydrate, in fractions of cell edges. Origin at a centre of symmetry.

	x	y	z
I	0.428	0.0783	0.3547
S	0.578	0.2192	−0.008
C	0.665	0.139	0.071
N_1	0.850	0.140	0.136
N_2	0.481	0.080	0.076
H_2O	0.250	0.250	0.214

In Tables 3 and 4, observed and calculated structure factors are listed for the 0*kl* zone of I and the *h*0*l* zone of II. In the temperature factor exp $[-B(\sin^2\Theta/\lambda^2)]$ applied to the calculated structure factors, the final values of B were chosen on the basis of the difference maps, and were as follows, in $Å^2$ units: In the 0*kl* zone of I, $B = 2.4$ for iodine, 2.2 for sulphur, and 2.6 for the lighter atoms, while in the *hk*0 zone, $B = 2.0$ for sulphur, 2.8 for the lighter atoms, and $2.4 + 1.4 \cos^2\varphi$ for iodine, where φ is the angle between the normal of the reflectiong plane and the direction of maximum vibration of the atom, the *a* axis. In the *h*0*l* zone of II, $B = 3.2$ for all atoms except bromine, where $B = 3.0 + 0.8 \cos^2\varphi$. Here, the direction of maximum vibration made an angle of about 44° with the *a* axis in the acute angle. In the 0*kl* zone of II, $B = 4.5$ for bromine, 2.0 for carbon and 4.0 for the other atoms.

The strong reflections, 060 of I and 200 and 302 of II have $|F_o|$ values markedly lower than the calculated ones. The two last reflections were omitted from the difference syntheses and the calculations of scale factor for the zone while the first one was, rather arbitrarily, included in the difference syntheses with half weight.

Table 2. Atomic coordinates for formamidinium disulphide dibromide monohydrate, in fractions of monoclinic cell edges. Origin at a centre of symmetry.

Coordinates used for final structure-factor calculations.

	(*h*0*l*)		(0*kl*)	
	x	*z*	*y*	*z*
Br	0.2925	0.0733	0.1310	0.0730
S	0.1200	0.2550	0.6500	0.2550
C	0.186	0.356	0.414	0.358
N_1	0.083	0.407	0.276	0.407
N_2	0.334	0.369	0.327	0.369
H_2O	0.500	0.250	0.706	0.250

Coordinates used to calculate interatomic distances and angles.

	x	*y*	*z*
Br	0.2925	0.1307	0.0727
S	0.1197	0.6502	0.2550
C	0.185	0.410	0.356
N_1	0.083	0.277	0.405
N_2	0.334	0.332	0.368
H_2O	0.500	0.711	0.250

The reliability index, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, with non-observed reflections included when $|F_c|$ exceeds the observable limit, is 0.089 and 0.097, respectively, for the 0*kl* and *hk*0 zones of the diiodide, and 0.068 for the *h*0*l* zone (0.076 if the above-mentioned 200 and 302 reflections with low observed values are included) and 0.098 for the 0*kl* zone of the dibromide.

In the space group *Pccn* of the diiodide, there is an uncertainty of $z = \frac{1}{4}$ with respect to location of symmetry centres which cannot be resolved from projections alone. That is because in the projection along the *a* as well as the *b* axis, symmetry centres, and twofold screw axes parallel to the projection axis and thus apparent symmetry centres, alternate at *c*/4 intervals along the *c* axis. Another uncertainty is that, once a set of coordinates for atoms of the disulphide cation has been chosen, there are two symmetry-related possibilities for the third coordinate of an iodide ion chosen in one projection. Both ambiguities can be resolved only by reference to *hkl* reflections with *l*

Table 3. Observed and calculated 0*kl* structure factors for formamidinium disulphide diiodide monohydrate.

k	F_o	F_c
	0*k*0	
2	75	+ 98
4	126	−143
6	304	−381
8	157	−156
10	34	+ 30
12	170	+159
14	202	+190
16	41	− 27
18	91	− 87
20	90	− 89
	0*k*2	
0	38	+ 33
1	105	+ 96
2	117	−116
3	239	+290
4	62	+ 53
5	220	+243
6	43	+ 53
7	64	− 60
8	36	+ 34
9	240	−250
10	< 26	+ 16
11	137	−130
12	85	− 78
13	< 32	+ 27
14	< 33	+ 17
15	116	+110
16	36	− 36
17	82	+ 77
18	45	+ 42
19	< 25	+ 21
20	< 20	− 2
	0*k*4	
0	269	−266
1	70	− 78
2	270	−262
3	215	−234
4	226	+217
5	82	− 72
6	191	+198
7	43	+ 34
8	148	+147
9	126	+121
10	< 28	− 12
11	83	+ 80
12	172	−163
13	< 33	− 6
14	104	− 92
15	69	− 66
16	< 32	− 26
17	54	− 58
18	94	+100
19	< 23	+ 1
20	40	+ 47
	0*k*6	
0	240	+228
1	86	− 86
2	45	+ 40
3	207	−199
4	< 23	− 13
5	145	−138
6	181	−163
7	60	+ 58
8	109	− 98
9	136	+137
10	34	+ 42
11	114	+110
12	73	+ 65
13	38	− 31
14	96	+ 96
15	64	− 62
16	< 30	− 26
17	73	− 72
18	< 24	− 22
19	< 19	+ 1
	0*k*8	
0	170	+157
1	149	+130
2	< 26	+ 14
3	173	+170
4	< 27	− 7
5	154	+144
6	118	−105
7	68	− 62
8	66	− 59
9	150	−142
10	< 33	+ 26
11	90	− 99
12	46	+ 37
13	< 33	+ 9
14	68	+ 70
15	85	+ 87
16	26	− 22
17	50	+ 62
18	< 18	− 12
	0,*k*,10	
0	159	−145
1	66	+ 47
2	149	−138
3	58	+ 55
4	117	+107
5	41	+ 44
6	134	+128
7	< 33	− 16
8	100	+ 99
9	45	− 55
10	< 33	− 13
11	< 32	− 21
12	101	−110
13	< 29	− 9
14	59	− 64
15	46	+ 34
16	< 20	− 15
17	< 14	+ 12
	0,*k*,12	
0	< 33	+ 26
1	< 33	− 32
2	< 33	− 20
3	147	−162
4	< 33	+ 10
5	74	− 82
6	< 33	− 10
7	< 33	+ 26
8	< 32	− 6
9	94	+114
10	< 30	+ 14
11	68	+ 77
12	< 26	− 14
13	< 33	− 24
14	22	+ 17
	0,*k*,14	
0	149	+156
1	< 30	+ 31
2	< 30	+ 38
3	< 30	+ 7
4	< 30	− 36
5	< 29	+ 18
6	94	−107
7	< 27	− 10
8	50	− 55
9	< 24	− 14
10	< 22	+ 12
11	< 18	− 6
	0,*k*,16	
0	28	− 20
1	32	+ 39
2	< 22	− 32
3	39	+ 55
4	< 21	+ 15
5	< 21	+ 15
5	49	+ 55
6	22	+ 31
7	< 15	− 18

Table 4. Observed and calculated $h0l$ structure factors for formamidinium disulphide dibromide monohydrate.

h	F_o	F_c
	$h00$	
1	10	+ 11
2	80	− 98
3	41	+ 43
4	4	+ 2
5	102	− 99
6	9	+ 7
7	44	+ 38
8	10	− 9
9	7	− 8
10	21	+ 22
	$h02$	
0	10	+ 10
1	71	− 79
2	12	− 7
3	114	+137
4	< 2	+ 3
5	37	− 35
6	44	+ 39
7	12	+ 11
8	52	− 52
9	6	− 7
10	10	+ 12
	$h0\bar{2}$	
1	4	+ 6
2	122	−128
3	12	+ 12
4	94	+ 91
5	7	+ 6
6	51	− 50
7	25	+ 22
8	< 3	+ 2
9	30	− 29
10	< 3	+ 1
	$h04$	
0	21	− 21
1	78	− 78
2	87	+ 88
3	11	+ 14
4	69	− 68
5	11	− 10
6	42	+ 38
7	12	− 10
8	< 3	− 2
9	26	+ 22
	$h0\bar{4}$	
1	112	+121
2	8	− 8
3	118	−119
4	31	+ 31
5	< 3	0
6	56	− 55
7	17	+ 17
8	55	+ 54
9	5	− 5
10	7	− 7
	$h06$	
0	123	−117
1	50	− 45
2	60	+ 58
3	8	− 5
4	26	− 26
5	64	+ 62
6	15	+ 14
7	39	− 38
8	4	− 4
9	13	+ 13
	$h0\bar{6}$	
1	47	+ 40
2	18	+ 19
3	52	− 47
4	20	+ 19
5	79	+ 77
6	3	− 2
7	23	− 22
8	6	+ 4
9	3	− 21
10	20	− 21
	$h08$	
0	13	− 11
1	59	+ 48
2	18	+ 15
3	73	− 69
4	20	− 20
5	17	+ 18
6	8	− 7
7	7	− 8
8	26	+ 24
	$h0\bar{8}$	
1	5	− 6
2	71	+ 69
3	15	− 14
4	49	− 50
5	16	+ 14
6	17	+ 17
7	32	− 34
8	6	+ 7
9	24	+ 25
10	3	− 4
	$h,0,10$	
0	26	− 26
1	42	+ 43
2	12	− 14
3	12	− 13
4	36	+ 36
5	9	+ 9
6	28	− 28
	$h,0,\overline{10}$	
1	54	− 54
2	26	+ 27
3	38	+ 38
4	24	− 23
5	8	+ 12
6	23	+ 23
7	14	− 16
8	18	− 21
9	5	+ 5
	$h,0,12$	
0	32	+ 35
1	16	+ 17
2	22	− 25
3	8	− 8
4	13	+ 16
5	11	− 13
	$h,0,\overline{12}$	
1	10	− 9
2	< 3	+ 1
3	16	+ 15
4	17	− 18
5	30	− 36
6	7	+ 7
7	11	+ 11
8	5	− 6
	$h,0,14$	
0	12	+ 13
1	9	− 11
2	9	− 11
3	17	+ 23
	$h,0,\overline{14}$	
1	8	− 9
2	26	− 31
3	8	+ 12
4	14	+ 16
5	4	− 6
6	2	+ 4

odd. In each case a choise was first made on the basis of calculated I—I and I—S distances, and the choise was later confirmed through comparison of calculated structure factors with rough intensity observations for a few representative *hkl* reflections.

ESTIMATE OF ERRORS

The standard deviations of atomic coordinates were estimated from the root-mean-square gradient of the difference maps and the curvature of the electron density peaks [28,29]. Where overlapping occurred, the s.d. was taken as about twice that which would otherwise have applied. In this way the following s.d. were obtained. In the diiodide, $\sigma(x) = 0.005$ Å, $\sigma(y) = \sigma(z) = 0.002$ Å for iodine; $\sigma(x) = \sigma(y) = \sigma(z) = 0.010$—0.012 Å for sulphur; $\sigma(x) = 0.04$—0.05 Å, $\sigma(y) = \sigma(z) = 0.02$—0.03 Å for carbon and nitrogen. In the dibromide, $\sigma(x) = \sigma(y) = 0.002$ Å, $\sigma(z) = 0.003$ Å for bromine; $\sigma(x) = \sigma(z) = 0.005$ Å, $\sigma(y) = 0.01$ Å for sulphur; $\sigma(x) = \sigma(z) = 0.015$—0.020 Å, $\sigma(y) = 0.03$—0.04 Å for carbon and nitrogen.

These values give standard deviations of 0.01 Å for the S—S bond length in the dibromide, and about 0.03 Å for S—C and C—N bond lengths. In the diiodide the corresponding figures are 0.02 Å and about 0.04 Å, respectively. For the S—S—C bond angle, $\sigma = 1°$ and 1—2°, and for S—C—N and N—C—N bond angles, about 2° and 3°, in the dibromide and diiodide, respectively. In both salts the S—S bond lies across a twofold axis, and the length is independent of the sulphur coordinate along the axis.

THE FORMAMIDINIUM DISULPHIDE ION

The salts are built up of disulphide cations and halide anions, and water of crystallization. The dimensions of the cation are listed in Table 5.

Table 5. Bond lengths and angles in the formamidinium disulphide ion.

	Diiodide	Dibromide		Diiodide	Dibromide
S—S	2.044 Å	2.044 Å	∠S—S—C	98.9°	104.0°
S—C	1.75	1.78	∠S—C—N_1	122.9°	121.2°
C—N_1	1.33	1.33	∠S—C—N_2	113.1°	118.3°
C—N_2	1.36	1.33	∠N_1—C—N_2	116.3°	119.0°
			Dihedral angle CSS/SSC	104.8°	89.2°

The S—S bond length is the same as in four other open-chain disulphides X—S—S—X for which data of comparable accuracy are available, namely 2.05 ± 0.02 Å in hydrogen disulphide [30], 2.04 ± 0.03 Å in dimethyl disulphide [30], 2.05 ± 0.02 Å in *bis*(trifluoromethyl) disulphide [31] and 2.04 ± 0.005 Å in N,N′-diglycyl-L-cystine dihydrate [32]. Also, the sulphur valency angle and the dihedral angle of the disulphide group lie in the normal range, *cf.* the recent review by Abrahams [33].

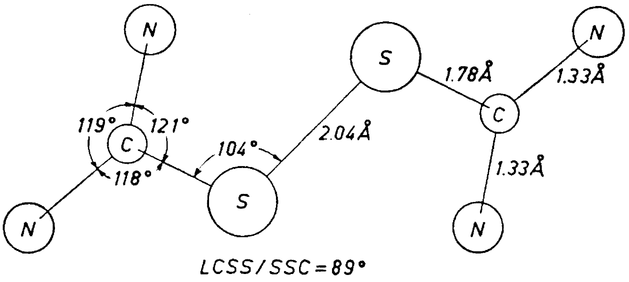


Fig. 5. The formamidinium disulphide cation as seen along the *b* axis of the dibromide.

The thiourea groups are planar within the accuracy of the atomic coordinates. Least squares planes through the four atoms of the group, with the sulphur coordinates given three times the weight of the carbon and nitrogen coordinates, have the equations

$$0.5340\ X - 0.4554\ Y - 0.7124\ Z = 0.023 \quad \text{(Diiodide)}$$
$$0.0573\ X + 0.6852\ Y + 0.7261\ Z = 4.582 \quad \text{(Dibromide)}$$

where X, Y and Z are in Å, in the case of the dibromide not referring to the axes of the monoclinic unit cell but to orthogonal axes a, b and c' where c' is normal to a and b. The planes pass at shortest distances of —0.006 Å from S, +0.083 Å from C, —0.036 Å from N_1 and —0.027 Å from N_2 in the diiodide, and at —0.007 Å from S, +0.068 Å from C, —0.022 Å from N_1 and —0.020 Å from N_2 in the dibromide. In view of the relatively large standard deviations of the coordinates of the lighter atoms, the displacements of the atoms from the planes can hardly be considered significant. On the other hand, it is known [34] that packing forces in crystals may cause distortions from planarity, of molecules or groups otherwise planar. As pointed out by Wheatley [35] with reference to ethylenethiourea, "distortions by crystal forces of molecules placed in unsymmetrical surroundings should be quite common". A decision is not possible in the present cases, although in the diiodide there is an indication that the distortion is real: As discussed later, the CN_1N_2 plane, $0.5548\ X - 0.6803\ Y - 0.5953\ Z = 0.001$, passes nearly equidistant between two iodide ions, and appears to allow a more reasonable location of amino hydrogen atoms than does the least-squares thiourea plane.

The two C—N bonds of a thiourea group have the same length, the slightly larger value for C—N_2 (1.36 Å) in the diiodide relative to the three other values of 1.33 Å being well within the experimental uncertainty. In fact, the thiourea groups are as in the thiourea molecule before oxidation of formamidinium disulphide, but for a slight but probably significant lengthening of the C—S bond relative to thiourea. According to a recent redetermination of the crystal structure of thiourea by Truter[36] the thiourea molecule is planar, with C—S = 1.710 ± 0.01 Å, C—N = 1.332 ± 0.01 Å, and ∠ N—C—N = 115°. The C and S atoms lie in a mirror plane which passes midway between the N atoms. Wheatley [35] found the same length, 1.708 ± 0.01 Å, for the C—S bond in ethylenethiourea, and deduced a value of 22 % double-bond character for a C—S bond of this length. Abrahams' bond length-bond order curve [33], based on 1.61 Å for a double and 1.82 Å for a single C—S bond, gives about 65 %. Although thus the bond order data are conflicting it seems certain that the C—S bond of thiourea possesses a considerable degree of double-bond character; whether or not some is retained in formamidinium disulphide cannot be decided on the basis of the rather inaccurate values of 1.75 Å and 1.78 Å for the bond, but appears probable since interaction of the lone electrons of sulphur (a $p\pi$ pair or one of two sp^3 π pairs) with the $p\pi$ orbital of the sp^2-hybridized carbon atom is still possible. The concerned sulphur and carbon π orbitals are approximately parallel, the normal of the SSC plane making an angle of 14° with the normal of the least-squares plane of the thiourea group in the diiodide, and 6° in the dibromide.

The relative orientation of the two thiourea groups of a formamidinium disulphide cation is slightly different in the two salts. Such differences may be expected to arise, from different packing forces in the crystals, and they manifest themselves in three ways: The sulphur valency angle is 99 ± 1—2° in the diiodide and 104 ± 1° in the dibromide. Although on the basis of the standard deviations the difference may not be real, the statistically more accurate S—S—G angles, where G is the centre of gravity of the thiourea group (the sulphur coordinates given three times the weight of those of the lighter atoms) are also different, namely 101° in the diiodide and 104° in the dibromide. Furthermore, a difference in the degree of rotation about the

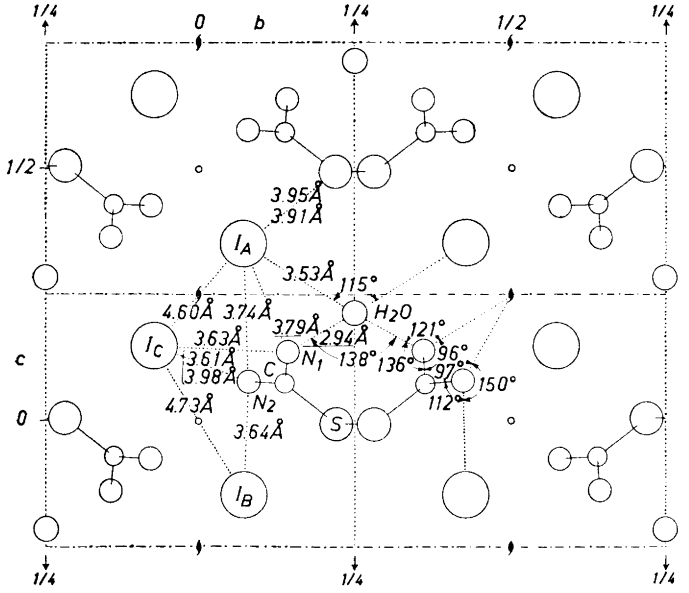


Fig. 6. The atomic arrangement in formamidinium disulphide diiodide monohydrate as seen along the *a* axis. Some non-bonded approaches and distances and angles relevant to the location of the hydrogen atoms are indicated.

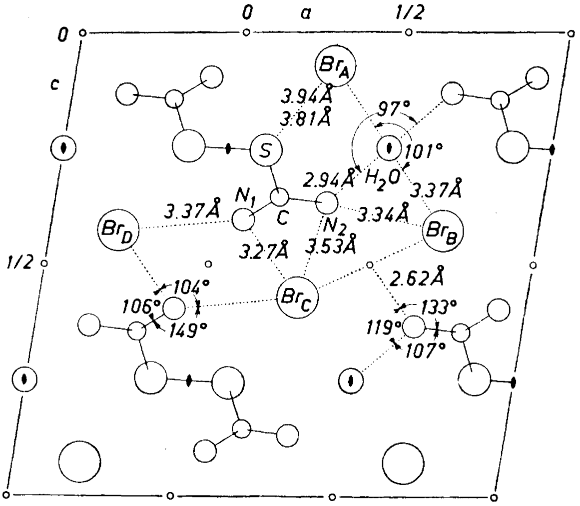


Fig. 7. A view along the *b* axis of the dibromide (one and a half unit cell) with interatomic approaches indicated as in Fig. 6.

S—S bond occurs, as expressed in the dihedral angles CSS/SSC which are 105° in the diiodide and 89° in the dibromide. Third, the sulphur atom of one thiourea group lies 0.48 Å from the least-squares plane of the other thiourea group in the diiodide and 0.22 Å in the dibromide, corresponding to different degrees of rotation, about the S—C bond, of the sulphur atom out of the plane.

THE PACKING IN THE CRYSTALS

The standard deviations of electron density, evaluated as the root-mean-square of the figures in the difference maps, are 0.46 and 0.65 e.$Å^{-2}$, respectively, for the *h*0*l* and 0*kl* zones of the dibromide, and 0.84 and 1.5 e.$Å^{-2}$, respectively, for the 0*kl* and *hk*0 zones of the diiodide. Any peak in the difference maps which might indicate positions of hydrogen atoms would therefore not be significant. In the following, the amino hydrogen atoms are assumed to be located in or not too far from positions corresponding to planar sp^2-hybridized nitrogen, as in urea and thiourea. They will be discussed with reference to the least-squares plane of the thiourea group in the dibromide, and to the CN_1N_2 plane in the diiodide, since this leads to slightly more reasonable hydrogen positions is some cases.

The atomic arrangements as seen along the shortest axis of each crystal are shown in Figs. 6 and 7.

Diiodide. The water molecule, located on a twofold axis at $\frac{1}{4},\frac{1}{4},z$ with $z = 0.214$, lies 3.53 Å from iodide ion I_A and the corresponding iodide ion on the other side of the twofold axis. The angle I—H_2O—I is 115°, and it seems probable that the water molecule forms hydrogen bonds to these iodide ions. Jellinek [37] reports a length of 3.57 Å for a O—H···I hydrogen bond in muscarine iodide. The same water molecule participates with its two lone electron pairs in N—H···O hydrogen bonding from two nitrogen atoms, at a distance of 2.94 Å and a N—H_2O—N angle of 138°. These nitrogen atoms are $N_{1(\bar{1}00)}$, in an adjacent unit cell along the *a* axis, and N_1', in the same unit cell but on the other side of the twofold axis, and belong to different formamidinium disulphide cations. This leads to the occurrence in the crystal of infinite helical chains parallel to the *a* axis, of alternating formamidinium disulphide cations and water molecules, with one of each per turn of the helix, and $a = 5.15$ Å as repeat distance. The C—N—H_2O angle is 136° and the oxygen atom lies 10°, as seen from the nitrogen atom, out of the CN_1N_2 plane. Each oxygen atom thus participates in four hydrogen bonds, with atoms which form a distorted tetrahedron about it; two of the relevant angles are given above and the other four are I—H_2O—N_1' = 120°, I—H_2O—$N_{1(\bar{1}00)}$ = 71°, and a corresponding pair on the other side of the twofold axis.

Each of the two iodide ions forms, in directions 87° and 67° away from the water molecule, close contacts (3.91 Å and 3.95 Å) with two sulphur atoms ($\angle$S—I—S = 82°) of an adjacent helix, related to the first through the operation of the glide plane *c* normal to the *a* axis. The sulphur atoms belong to different disulphide cations, in adjacent unit cell along the *a* axis. Four such I—S contacts occur per turn of the helix, one of each length on each side of the twofold axis. Each iodide ion also forms two fairly close contacts with other iodide ions, in directions away from the helixes, namely 4.60 Å over the nearest screw axis parallel to the *a* axis, and 4.73 Å over the nearest symmetry centre.

One of the four amino hydrogen atoms of each thiourea group has so far been accounted for, through hydrogen bonding to water. There are short approaches between the nitrogen atoms and the iodide ions I_A and I_C (at $\frac{1}{2} + x, \bar{y}, \frac{1}{2}—z$; related to I_A through the operation of the screw axis at $x,0,\frac{1}{4}$): N_1—I_A = 3.79 Å, N_1—I_C = 3.63 Å, N_2—I_A = 3.74 Å, N_2—I_C = 3.61 Å. Expected length of a N—H···I hydrogen bond would be in this range, judging from values listed for N—H···Cl bonds [38]. However, I_A lies — 2.36 Å and I_C lies + 2.24 Å out of the CN_1N_2 plane, so that linear hydrogen bonds are improbable *. Now, the line joining I_A and I_C is normal to the CN_1N_2 plane (I_A—I_C = 4.60 Å), and the midpoint P between I_A and I_C, on the screw axis, is only —0.06 Å out of the plane, and 2.91 Å from N_1 and 2.86 Å from N_2. It appears likely that one N_1—H and one N_2—H bond are directed, not towards I_A or I_C but towards their midpoint, or nearly so. The relevant angles at N_1 and N_2 are: C—N_1—P = 96°, $H_2O_{(100)}$—N_1—P = 121°, C—N_2—P = 97°. With a N—H bond length of 1.0 Å the hydrogen atoms would lie 2.9—3.0 Å from the iodide ions, each hydrogen atom forming two such contacts.

It remains to account for one N_2 hydrogen atom. N_2 lies 3.64 Å from I_B (at $\frac{1}{2}—x, y, z—\frac{1}{2}$, related to I_A through the glide plane *c* at $x = \frac{1}{4}$) and 3.98 Å from $I_{C(\bar{1}00)}$. These two iodide ions are 4.73 Å apart, and are related through the symmetry centre at the origin. Both lie 0.62 Å out of the CN_1N_2 plane, their midpoint Q (the origin) lies in the plane and 2.99 Å from N_2. There are

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* The distances from I_A and I_C to the least-squares plane of the thiourea group are —2.82 Å and +1.73 Å. The midpoint between I_A and I_C lies —0.54 Å out of the least-squares plane.

then two directions of the second N_2—H bond to consider, namely, towards I_B or towards the midpoint Q between I_B and $I_{C(\bar{1}00)}$. The angles, C—N_2—I_B = 112°, P—N_2—I_B = 150°, C—N_2—Q = 112°. It appears that a direction intermediate between these two would give reasonable valency angles at N_2.

Dibromide. The expected lengths of N—H···Br and O—H···Br hydrogen bonds, from analogous bonds involving chloride, are about 3.3 Å.

The environment of the water molecule is as in the diiodide. The molecule lies on a twofold axis, at $\frac{1}{2},y,\frac{1}{4}$ with $y = 0.711$, and participates in hydrogen bonding to two bromide ions, above, and from two amino nitrogen atoms, below as seen down the twofold axis, one of each kind on each side of the axis, and in an approximately tetrahedral arrangement. The bromide ions are $Br_{A(010)}$, in an adjacent cell along the *b* axis, and $Br_{B(010)}$, related to the first through the twofold axis. The coordinates of Br_A are those listed in Table 2. The distances O—H···Br = 3.37 Å and N_2—H···O = 2.94 Å, and the angles, Br—H_2O—Br = 101°, N_2—H_2O—N_2 = 97°, $Br_{A(010)}$-H_2O-N_2 = 120° and $Br_{B(010)}$—H_2O—N_2 = 110°. The angle C—N_2—H_2O is 107°, and the water molecule is 0.35 Å out of the least-squares plane of the thiourea group, or 7° as seen from N_2. Again the N—H···O hydrogen bonds lead to the occurrence of an infinite chain, parallel to the *a* axis, of alternating water molecules and formamidinium disulphide cations. The water molecules and the sulphur atoms of the cations lie approximately on a straight line, at $y = 0.65$—0.71 and $z = \frac{1}{4}$, with the N_2 atoms below at $y = 0.332$ and the bromide ions above at $y = 1.131$, on both sides of $z = \frac{1}{4}$. The distances from Br_A and $Br_{A(010)}$ to the sulphur atom of the thiourea group to which N_2 belongs are 3.94 Å and 3.81 Å, respectively.

The nitrogen atom N_2 lies 3.34 Å and 3.53 Å, respectively, from the bromide ions Br_B and Br_C, these two ions are 4.46 Å apart and are related through the symmetry centre P at $\frac{1}{2},0,\frac{1}{2}$, they lie —0.03 Å and + 0.12 Å, respectively, out of the least-squares plane of the thiourea group. The geometry is, however, not favourable for N—H···Br hydrogen bonding, the angle C—N_2—Br_B being 173°, H_2O—N_2—Br_B = 77°, C—N_2—Br_C = 94° and H_2O—N_2—Br_C = 156°. The symmetry centre P, midway between the bromide ions, is 2.62 Å from N_2 and 0.05 Å out of the least-squares plane, and the angle C—N_2—P = 133° and H_2O—N_2—P = 119°. It appears probable that a N_2—H bond is directed towards the symmetry centre, the hydrogen atom would then lie about 2.75 Å from both bromide ions.

The other nitrogen atom of the thiourea group, N_1, lies 3.27 Å and 3.37 Å, respectively, from the bromide ions Br_C and Br_D, related to each other through a symmetry centre at $0,0,\frac{1}{2}$. They are 0.12 Å and — 0.54 Å, respectively, out of the least-squares plane, or 2° and 9° as seen from N_1. The angles, C—N_1—Br_C = 106°, Br_C—N_1—Br_D = 104°, C—N_1—Br_D = 150°, are not quite satisfactory for hydrogen bonding; the valency angles at N_1 would become more equal if the two N_1—H bonds are directed not towards the bromide ions but slightly aside of the ions.

A hydrate structure analogous to the two present ones occurs in adenine hydrochloride hemihydrate[39], where the water molecule lies on a twofold axis with two chloride ions (O—H···Cl = 3.12 Å) and two nitrogen atoms (O···H—N = 2.87 Å) in a distorted tetrahedral arrangement about it.

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