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The Crystal Structure of Piperazinium Di-dichloroiodide

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The crystal structure of piperazinium di-dichloroiodide, $C_4H_{10}N_2 \cdot 2(HCl \cdot ICl)$, has been determined by X-ray methods. The ICl_2^-ion, being linear but not symmetrical, has the configuration $Cl^- - I - Cl$ with the $Cl^- - I$ distance 2.69 Å and the $I - Cl$ distance 2.47 Å. The Cl^- is coordinated to three positive groups and one iodine atom in a distorted tetrahedral arrangement, the three $N+ - Cl^-$ distances being 3.23 Å.

It has been known for a long time that addition compounds between an amine and one halogen molecule form compounds with one molecule hydrogen halide. In the course of an investigation carried out in this department of the former type of addition compounds[1] it was thought to be of interest to examine one of the hydrogen halide compounds. The choice of the present compound, piperazine with two molecules ICl and two molecules HCl added to it, was made because of its centrosymmetrical configuration.

Earlier structure determinations of this type of compounds include $NH_4 \cdot I_3$[2], $NH_4 \cdot ClIBr$[3] and $(CH_3)_4N \cdot ICl_2$[4]. The structure of the trihalide ions is discussed by Hach and Rundle[5].

EXPERIMENTAL

Piperazinium di-dichloroiodide was prepared by adding a solution of iodine monochloride in hydrochloric acid to a hot solution of piperazine in water. After slow cooling to room temperature small yellow needle-formed crystals of the compound separated from the solution. Oscillation and Weissenberg photographs about two crystallographic axes were taken in order to determine the unit cell dimensions. The $(0kl)$-intensities were estimated visually from a set of Weissenberg films while the $(hk0)$-intensities were measured microphotometrically from photographs taken with a Wiebenga integrating Weissenberg camera. The crystals used had a cross-section of 0.10 × 0.10 mm. Copper $K\alpha$ radiation was employed ($\lambda = 1.542$ Å). 103 $(0kl)$-reflections out of 114 obtainable with this radiation and 113 $(hk0)$-reflections out of 131 possible were recorded. Absorbtion corrections were not applied.

CRYSTAL DATA

The crystals were found to be triclinic with the unit cell dimensions:

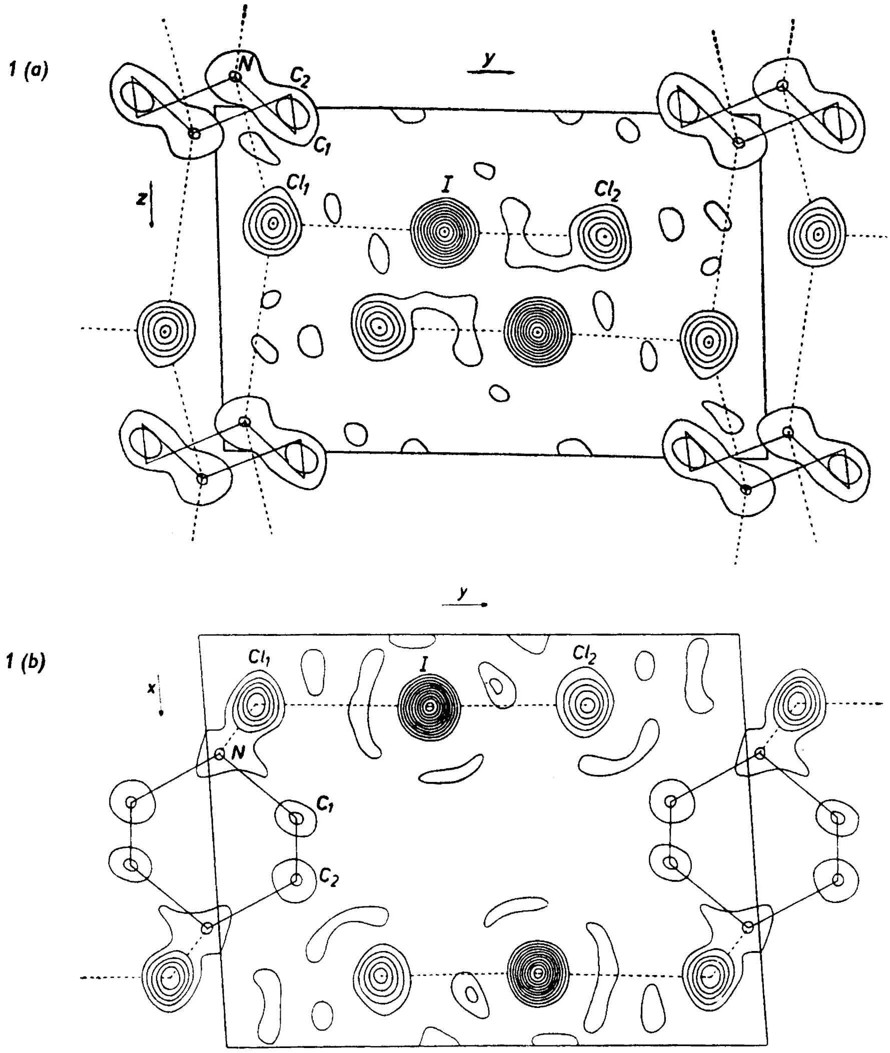

Fig. 1. Electron density projection along the *a*-axis (a) and *c*-axis (b). Contours at intervals of 5 e·Å^{-2}. Every second contour in the iodine peak is omitted.

$a = 7.55$ Å $b = 8.45$ Å $c = 6.25$ Å
$\alpha = 87.6°$ $\beta = 121.8°$ $\gamma = 84.4°$

The figures given are believed to be accurate to within 0.5 % for the axial lengths and 0.5° for the angles.

The density was determined from flotation experiments and was found equal to 2.33 g/cm^3. With one molecule in the unit cell the calculated density is 2.38 g/cm^3.

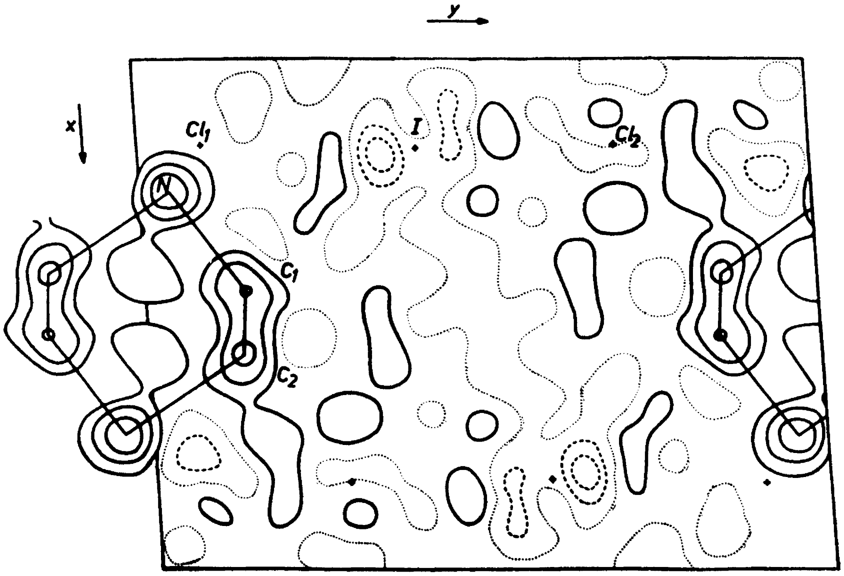

Fig. 2. ($F_0 - F_{\text{hal}}$) projection along the c-axis. Contours at intervals of 2 e.Å^{-2}. Negative contours are broken and zero contour dotted. The halogen positions are indicated by crosses.

The space group P$\bar{1}$ was assumed to be the correct one as a centre of symmetry has previously been observed to exist in the piperazine ring, suggesting a symmetrical distribution of the (HCl.ICl) groups with respect to the two nitrogen atoms.

THE STRUCTURE DETERMINATION

Projection along the c-axis. Approximate x and y parameters for the iodine atom were determined by inspection of the (h00)- and (0k0)-reflections, and the signs for the structure factors based on these parameters were evaluated. A preliminary Fourier synthesis resulted in an electron density map showing well separated peaks for the iodine and the two chlorine atoms in the asymmetric unit. The position of the piperazine ring around the symmetry centre in (0,0) was also roughly indicated. After two refinements the electron density map of Fig. 1(a) was obtained, showing the halogen and nitrogen positions, whereas the two carbon atoms are too close together to be resolved as separate peaks.

Projection along the a-axis. The determination of this projection was carried out independently, using the same methods. The Fourier map obtained after three refinements is given in Fig. 1(b), showing all the atoms as separate peaks. The termination of series error introduces positive areas around the heavy atoms, and this effect is seen to have some influence on the position of the nitrogen peak. In order to find more precise parameters for this atom

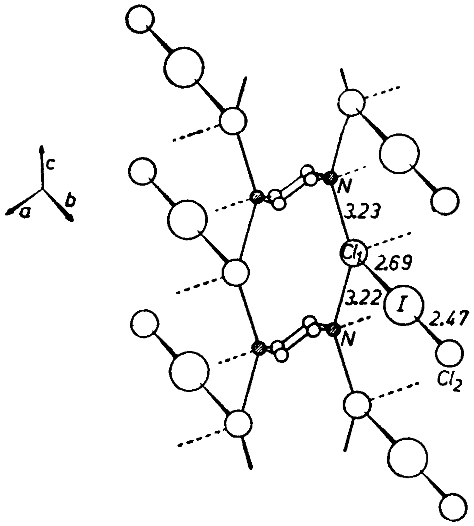

Fig. 3. Structure of piperazinium di-dichloroiodide. The figure shows a few of the units in a chain of piperazinium ions and ICl_2^- ions along the *c*-axis. The broken lines indicate the bonds between neighbouring chains. Bond lengths are in Å units.

a (F_0—F_{hal}) synthesis [6] was carried out, F_0 is the observed structure factor and F_{hal} is the contribution to the calculated structure factor from the halogen atoms alone. The difference map is given in Fig. 2. The nitrogen atom is now closer to the Cl_1 atom, but the positions of the carbon atoms remain nearly the same as before. The gradients at the halogen positions are too small to indicate any adjustments of the parameters.

The y parameters found for the halogen atoms in the two projections agree to within 0.001 of the axial length. For the nitrogen atom the difference is 0.006. The z parameters for the carbon atoms were calculated using x and y parameters found in the (F_0—F_{hal}) synthesis and assuming the carbon-carbon distance across the ring through the symmetry centre to be 1.90 Å. The atomic coordinates are given in Table 1.

Table 1. Atomic coordinates as fractions of the cell edges.

Atom	x	y	z
I	0.177	0.416	0.362
Cl_1	0.169	0.099	0.341
Cl_2	0.168	0.709	0.366
N	0.277	0.040	−0.086
C_1	0.455	0.148 *	0.082 *
C_2	0.582	0.140 *	−0.036 *

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* The mean value of the y and calculated z parameters are 0.144 and 0.023, respectively, whereas the common maximum in the a-projection has the parameters 0.140 and 0.017.

Table 2. Bond lengths in trihalide ions.

Compound	Bond type	Bond length	Sum of covalent radii	Reference
NH_4ClIBr	I–Cl	2.38 Å	2.32 Å	3
	I–Br	2.50 Å	2.47 Å	3
$(CH_3)_4NICl_2$	$I-Cl_1$	2.34 Å	2.32 Å	4
	$I-Cl_2$	2.34 Å	2.32 Å	4
$PICl_6$	$I-Cl_1$	2.36 Å	2.32 Å	10
	$I-Cl_2$	2.36 Å	2.32 Å	10
NH_4I_3	I_1-I_2	3.10 Å	2.66 Å	2
	I_2-I_3	2.82 Å	2.66 Å	2
CsI_3	I_1-I_2	3.04 Å	2.66 Å	11
	I_2-I_3	2.86 Å	2.66 Å	11
$C_4H_{12}N_2 \cdot 2ICl_2$	$I-Cl_1$	2.69 Å	2.32 Å	Present
	$I-Cl_2$	2.47 Å	2.32 Å	examination

Observed and calculated structure factors are listed in Table 3. For the 12 largest (marked with an asterisk) the observed values are seen to be considerably lower than the calculated ones. This effect is thought to be mainly due to extinction, and these reflections are therefore disregarded in the calculation of the reliability index and the $(F_0—F_{\mathrm{hal}})$ synthesis. They are, however, included in the estimations of the standard deviations.

For the different atoms the following B values in the temperature factor exp $(—B \sin^2 \Theta / \lambda^2)$ were used:

$(0kl)$- reflections: $B_{\mathrm{I}} = 2{\cdot}0$ Å^2; $B_{\mathrm{Cl}} = 2.5$ Å^2; $B_{\mathrm{N\ and\ C}} = 3.0$ Å^2
$(hk0)$-reflections: $B_{\mathrm{I}} = 1{\cdot}5$ Å^2; $B_{\mathrm{Cl}} = 2.0$ Å^2; $B_{\mathrm{N\ and\ C}} = 2.5$ Å^2

The atomic scattering factors given in *Internationale Tabellen* [7] were used in the calculations. The reliability index R is 0.11 for the $(0kl)$-reflections and 0.12 for the $(hk0)$-reflections.

Estimates of the standard deviations [8] for the halogen positions were as follows:

I: $\sigma(x) = 0.002$ Å; $\sigma(y) = 0.003$ Å; $\sigma(z) = 0.003$ Å
Cl: $\sigma(x) = 0.008$ Å; $\sigma(y) = 0.012$ Å; $\sigma(z) = 0.010$ Å

The standard deviation for the nitrogen coordinates is 0.06 Å.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal may be regarded as being built up of chains running parallel to the *c*-axis, as shown in Fig. 3. In every chain piperazinium ions alternate with ICl_2^- ions. In such a chain a chlorine atom like Cl_1 is coordinated to *two* equivalent nitrogens. The nitrogen and Cl_1 atoms in one chain are coordinated to Cl_1, respectively nitrogen atoms in a neighbouring chain to form a net paral-

Table 3. Observed and calculated structure factors. The given values are one half of the absolute values. F_0's suffering from extinction are marked with an asterisk.

hkl	F_0	F_c
100	29.1	26.6
200	31.5 *	−38.8
300	39.0	−53.8 *
400	13.3	−13.0
500	23.2	25.0
600	24.1	26.5
700	8.3	6.0
800	13.3	−16.5
010	13.7	−22.5
020	14.8	18.1
030	2.9	2.5
040	23.4	−23.0
050	11.4	11.8
060	30.2	−29.1
070	26.2	26.4
080	12.5	−8.8
090	< 3.4	−1.3
0.10.0	12.0	9.7
001	23.0 *	−35.3
002	5.1	−6.3
003	40.9	42.3
004	30.8	−32.9
005	7.4	6.2
006	9.7	9.2
011	16.5	16.8
012	19.4	21.6
013	20.5	−22.4
014	10.8	12.4
015	< 3.4	−0.7
016	8.6	−7.4
$01\bar{1}$	30.2 *	46.7
$01\bar{2}$	6.8	−8.4
$01\bar{3}$	12.5	−13.2
$01\bar{4}$	24.5	21.6
$01\bar{5}$	15.4	−15.6
$01\bar{6}$	< 2.8	−0.9
021	6.3	8.2
022	19.4	−20.3
023	16.5	20.1
024	6.3	−5.6
025	8.5	−7.9
026	9.1	11.1
$02\bar{1}$	20.0	−21.6
$02\bar{2}$	12.0	15.6
$02\bar{3}$	< 2.8	−1.3
$02\bar{4}$	12.5	−10.0
$02\bar{5}$	8.6	8.9
$02\bar{6}$	3.4	−6.5
031	37.0 *	−44.9
032	37.5	47.9 *
033	14.8	−16.4
034	15.4	−15.4
035	19.4	22.0
036	14.8	−14.3
$03\bar{1}$	28.0 *	36.0
$03\bar{2}$	28.6 *	−47.7
$03\bar{3}$	15.4	17.1
$03\bar{4}$	6.8	7.0
$03\bar{5}$	20.5	−19.4
$03\bar{6}$	12.0	12.9
041	31.4	35.2
042	23.4	−22.5
043	< 3.4	1.1
044	13.7	14.4
045	12.5	−14.0
046	3.4	5.9
$04\bar{1}$	14.8	−14.5
$04\bar{2}$	26.8	27.6
$04\bar{3}$	27.4	28.1
$04\bar{4}$	< 3.4	2.6
$04\bar{5}$	8.6	10.5
$04\bar{6}$	13.7	13.7
051	17.1	−16.0
052	13.7	12.6
053	3.4	4.2
054	9.7	−10.1
055	8.0	9.6
056	2.9	−3.1
$05\bar{1}$	2.9	−0.1
$05\bar{2}$	16.0	−13.4
$05\bar{3}$	10.3	9.4
$05\bar{4}$	5.7	−6.4
$05\bar{5}$	4.6	−1.9
061	19.4	19.3
062	12.0	11.3
063	20.5	−21.5
064	17.1	18.7
065	< 2.8	−3.1
$06\bar{1}$	23.9	21.3
$06\bar{2}$	< 3.3	1.9
$06\bar{3}$	18.2	−17.7
$06\bar{4}$	14.8	15.0
$06\bar{5}$	4.0	−5.5

hkl	F_o	F_c
071	< 3.4	1.6
072	17.7	−15.7
073	21.1	20.7
074	6.8	− 8.3
075	4.0	− 3.3
07$\bar{1}$	32.5	−25.1
07$\bar{2}$	14.3	12.4
07$\bar{3}$	8.6	8.0
07$\bar{4}$	17.1	−17.2
07$\bar{5}$	10.3	12.3
081	3.4	1.0
082	9.1	9.3
083	10.8	−10.1
084	6.8	5.8
08$\bar{1}$	16.5	12.2
08$\bar{2}$	5.1	− 5.9
08$\bar{3}$	< 2.8	− 1.6
08$\bar{4}$	7.4	6.6
091	11.4	11.1
092	14.8	−13.9
093	5.7	5.7
094	3.4	5.5
09$\bar{1}$	13.7	−11.2
09$\bar{2}$	12.5	11.0
09$\bar{3}$	4.0	− 5.2
0.10.1	17.7	−16.5
0.10.2	7.4	7.9
0.10.$\bar{1}$	< 2.2	0.2
0.10.$\bar{2}$	13.1	−13.1
110	24.1 *	−38.6
210	< 4.2	4.0
310	24.9	31.1
410	19.9	18.6
510	10.0	− 9.6
610	17.4	−17.6
710	8.3	− 6.5
$\bar{1}$10	5.8	− 2.8
$\bar{2}$10	22.4	30.8
$\bar{3}$10	19.1	21.2
$\bar{4}$10	9.1	− 5.4
$\bar{5}$10	17.4	−19.5
$\bar{6}$10	11.6	−11.3
$\bar{7}$10	8.3	8.7
120	21.6	24.5
220	< 3.3	1.0
320	13.3	−14.1
420	15.8	−16.7
520	< 5.8	− 2.1
620	14.9	16.7
720	9.1	8.4
$\bar{1}$20	8.3	−10.3
$\bar{2}$20	21.6	−26.8
$\bar{3}$20	7.5	− 6.6
$\bar{4}$20	11.6	15.1
$\bar{5}$20	15.8	13.2
$\bar{6}$20	< 6.6	− 1.2
$\bar{7}$20	6.6	− 7.9
130	31.5 *	−47.9
230	36.5 *	−50.7
330	9.1	7.3
430	34.0	36.0
530	21.6	22.6
630	< 6.6	− 4.4
730	19.9	−21.0
$\bar{1}$30	39.8 *	58.7
$\bar{2}$30	25.7	33.7
$\bar{3}$30	11.6	− 9.6
$\bar{4}$30	25.7	−35.0
$\bar{5}$30	19.1	−20.6
$\bar{6}$30	7.5	8.7
$\bar{7}$30	19.1	19.8
140	18.3	20.8
240	27.4	34.2
340	15.8	15.6
440	18.3	−19.1
540	26.6	−24.5
640	< 5.8	− 3.2
740	13.3	13.3
$\bar{1}$40	28.2	−32.3
$\bar{2}$40	15.8	−16.1
$\bar{3}$40	17.4	20.3
$\bar{4}$40	23.2	25.9
$\bar{5}$40	< 6.6	3.0
$\bar{6}$40	11.6	−13.7
$\bar{7}$40	12.5	−13.8
150	11.6	− 9.1
250	15.8	−18.2
350	5.6	− 6.5
450	9.1	9.1
550	13.3	12.8
650	< 5.8	4.3
750	5.8	− 7.0
$\bar{1}$50	19.9	19.2
$\bar{2}$50	< 5.8	− 0.7
$\bar{3}$50	14.1	−12.5
$\bar{4}$50	9.1	− 7.7
$\bar{5}$50	5.8	2.7
$\bar{6}$50	8.3	8.4

hkl	F_o	F_c
160	23.2	−21.6
260	18.3	18.0
360	26.6	28.5
460	10.0	8.5
560	15.8	−14.1
660	18.3	−18.2
$\bar{1}60$	11.6	−10.8
$\bar{2}60$	20.8	19.9
$\bar{3}60$	24.9	24.2
$\bar{4}60$	8.3	5.0
$\bar{5}60$	14.1	−14.8
$\bar{6}60$	16.6	−15.3
170	26.6	25.6
270	< 6.6	2.3
370	22.4	−22.6
470	20.8	−20.2
570	< 5.8	2.3
670	14.1	16.5
$\bar{1}70$	9.1	− 6.1
$\bar{2}70$	26.6	−25.3
$\bar{3}70$	19.9	−17.5
$\bar{4}70$	6.6	7.7
$\bar{5}70$	20.8	19.2
180	17.4	−14.4
280	< 6.6	1.4
380	14.9	12.5
480	10.0	9.6
580	< 5.0	− 2.3
$\bar{1}80$	< 6.6	5.2
$\bar{2}80$	14.1	12.4
$\bar{3}80$	8.3	4.8
$\bar{4}80$	5.8	− 5.4
190	15.8	14.8
290	15.8	14.6
390	< 5.0	− 1.9
490	15.8	−13.9
590	8.3	− 8.9
$\bar{1}90$	15.8	−18.8
$\bar{2}90$	11.6	−12.0
$\bar{3}90$	< 4.1	4.1
1.10.0	< 5.0	− 5.2
2.10.0	21.6	−18.9
3.10.0	11.6	− 9.5
$\bar{1}$.10.0	21.6	19.1

lel to the *a*-*c* plane. The bonds between the chains are indicated in Fig. 3 by broken lines. The ICl_2^- ions are linear and their direction approximately normal to the net. In Fig. 4 is shown a projection of the structure along the chain axis (*c*-axis), the broken lines here too indicating the bonds between the chains.

Cl_1 is surrounded by three nitrogens and one iodine atom in a distorted tetrahedral arrangement. The distance to the nitrogen atoms are 3.22 Å, 3.23 Å and 3.25 Å, respectively, as indicated in the figures. The angles N-Cl_1-N are 152°, 122° and 122° and the angles N-Cl_1-I are 102°, 95° and 120°. The Cl_1-N distances are somewhat shorter than the distance found in ammonium chloride (3.35 Å), but are equal to the shortest Cl-N distance observed in ammonium chlorobromoiodide [3].

As may be seen from Fig. 4 the distance between the Cl_2 atom in one net and the Cl_1 atom in the next one is only 3.29 Å and the shortest I—I separation is 4.06 Å while the sum of the van der Waals radii as given by Pauling [9] are 3.60 Å and 4.30 Å, respectively. These short intermolecular distances indicate a comparatively strong interaction between the nets, and the forces here are probably mainly responsible for the packing of the nets along the *b*-axis into the three dimensional lattice. All other intermolecular distances are found to be larger than the sums of the van der Waals radii.

The N—N′ distance across the piperazine ring as calculated from the coordinates given above is 2.94 Å which is close to the expected value.

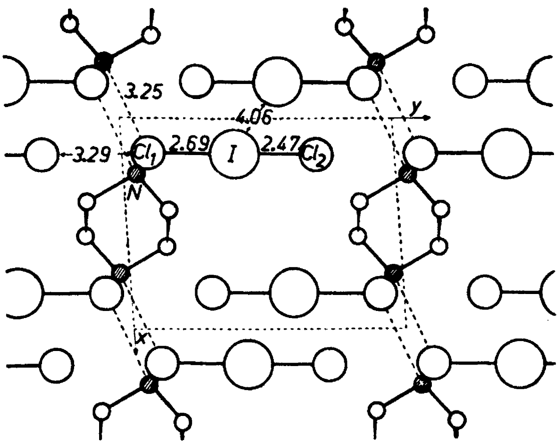

Fig. 4. The structure as seen along the chain axis. The broken lines denote the connection between the chains as in Fig. 3. Distances are in Å units.

The three halogen atoms form a linear (Cl—I—Cl)$^-$ ion which, however, is unsymmetrical, the Cl_1-I distance being 2.69 Å and the I-Cl_2 distance 2.47 Å. Since the standard deviation for the Cl-I distance is only 0.012 Å the difference between the two distances is certainly significant. Both of the I-Cl distances are substantially larger than the sum of the covalent radii[9] (2.32 Å), and also larger than the distances found in earlier examinations of the ICl_2^- ion. The halogen-halogen distances so far determined in X-ray examinations of trihalides are listed in Table 2.

Since the Cl_1 atom is surrounded closely by the positive ammonium groups while the distance from Cl_2 to the nearest nitrogen is 4.30 Å it seems very probable that Cl_1 carries a negative charge. The present ion is more analogous to the I_3^- ion than to the earlier examined ICl_2^- and $ClIBr^-$ ions as may be seen from Table 2.

It appears natural to describe the present ion as an addition complex between an electron donor (Cl^-) and an electron acceptor (ICl) and to suggest that the bond is of the same type as in the addition compounds between amines and halogens[1]. The I-Cl distance in pyridine · ICl is thus very nearly the same as in the present Cl^--I-Cl ion, and it may also be mentioned that the I-I distance found in the addition compound between benzyl sulphide and I_2[1] corresponds closely to the shorter one in the I_3^- ion.

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