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Crystal Structure of the 1:1 Addition Compound Trimethylamine — Iodo Monochloride

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As a part of a research programme dealing with the structures of charge transfer compounds having halogen molecules as electron acceptors the crystal structure of the 1:1 compound trimethylamine — iodo monochloride has been determined. The crystals are orthorhombic, the space group is *Pbca* and the lattice constants:

$a = 11.52$ Å $\quad b = 11.08$ Å $\quad c = 10.77$ Å

The number of molecules per unit cell is *eight*.

The nitrogen atom is tetrahedrally surrounded by the methyl groups and the I—Cl group, the N—I—Cl arrangement is at least nearly linear. The N—I distance (2.30 Å) corresponds closely to the distance previously observed in addition compounds formed by tertiary amines, the I—Cl distance of 2.52 Å is very nearly the same as that observed in the pyridine iodo monochloride compound (2.54 Å).

During the last few years crystal structure determinations of a series of charge transfer compounds have been carried out in this laboratory in which halogen molecules act as acceptors; ethers, amines and different other organic molecules as donors. The following report deals with the 1:1 compound formed by trimethylamine and iodo monochloride.

This compound (apparently first described as a simple addition compound by Pictet and Krafft [1]) is easily obtained by bringing together equimolecular quantities of the two components dissolved in a non-polar solvent like ligroin, carbon disulphide or carbon tetrachloride at temperatures below 10°C. We used the latter solvent and added the iodo monochloride solution drop by drop to the amine solution which was cooled by ice water. The yellow precipitate was dried *in vacuo* in the dark and stored at a low temperature. It was recrystallized from methylene chloride at temperatures below 10°C.

Analysis of the compound was carried out as follows: The substance was dissolved in glacial acetic acid and solid potassium iodide added, thereafter water in portions. Free iodine was titrated with a standard thiosulphate solution. The results obtained correspond within one per cent to theoretical values for $(CH_3)_3NICl$. Combustion analysis gave the following result: Found C 16.2; H 3.9. Calc. for C_3H_9NICl: C 16.3; H 4.1.

Single crystals were grown from methylene chloride solution by slowly evaporating the solvent in a refrigerator box. The most ideally developed crystals were obtained by

putting fine glass fibres into the vessel in which the crystals were grown. The crystals thus obtained were firmly fixed to the fibre and could be mounted on the goniometer head of the camera and set in the desired position. In cases where the linear extension of the crystal exceeded 0.1 mm its dimensions could be reduced by repeatedly bringing it for a short time into methylene chloride. Although the crystals are not very stable even at room temperature, the first Weissenberg pictures intended for a determination of lattice constants and space group could be obtained without cooling the crystals or putting them into sealed capillary tubes. Later exposures used for intensity measurements were performed at about −20°C in a Weissenberg camera equipped with cooling devices. The multiple film technique was employed and the intensities estimated visually. All diagrams were taken with CuK radiation.

The crystals are orthorhombic, bipyramidal in shape, the space group is *Pbca*. The lattice constants are as follows (−20°C):

$$a = 11.52 \text{ Å}; \qquad b = 11.08 \text{ Å}; \qquad c = 10.77 \text{ Å}$$

with a possible error of ± 0.5 %. Inserting the density measured at room temperature (2.10 g cm^{-3}) the calculated number of molecules in the unit cell is 7.84.

The number of observed reflexions in the *hk0* zone was 68 (theor. 82), in the *0kl* zone 69 (theor. 82) and in the *h0l* zone 61 (theor. 83).

The plane group of all three projections along the principal axes is the same, *pgm*. The first of these projections to be worked out was that along the z-axis (Fig. 1). The structure factor signs were computed on the basis of a Patterson synthesis and a Fourier synthesis subsequently worked out. The y parameter of chlorine, determined from the Fourier map, was not very accurate, however, because of overlapping, and the next step was the working out of a synthesis with projection along the x axis (Fig. 2). The coordinates of both iodine and

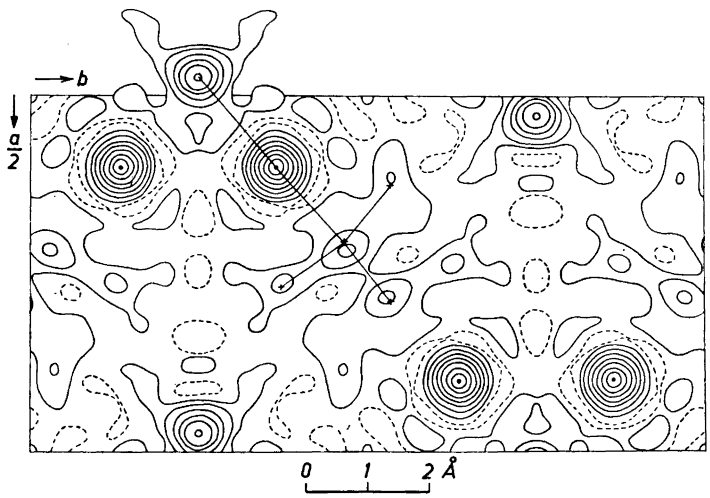

Fig. 1. Fourier projection along the z-axis. Contour lines for I at 0, 5, 20, 35, ... eÅ^{-2}, for Cl at 0, 5, 10, 20... eÅ^{-2}, for lighter atoms at 0, 5, 10, 15... eÅ^{-2}.

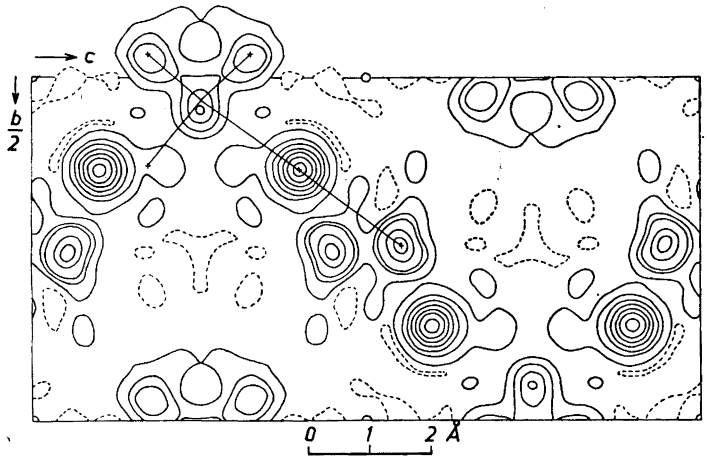

Fig. 2. Fourier projection along the x-axis. Contour lines for I at 0, 5, 20, 35... eÅ^{-2}, for all other atoms at 0, 5, 10, 15... eÅ^{-2}.

chlorine atoms were thus determined, but due to overlapping the x and z coordinates of the nitrogens were still rather uncertain and a Fourier projection along the y axis was therefore carried out inserting the structure factor signs obtained from the two first projections.

For all three projections difference Fourier projections were worked out with subtraction of the contribution from iodine.

The atomic coordinates arrived at by combining the information obtained from all the projections are listed in Table 1.

The agreement between observed and calculated structure factors may be judged by inspecting Table 2. When calculating the values listed in this table a temperature factor $B = 2.40$ was employed which was independently derived both from the xy and the yz projection. The "reliability factor" R including all observed reflexions is 0.09.

The agreement between observed and calculated intensities appears to be good enough to garantee that the iodine coordinates and even the chlorine coordinates have been determined with considerable accuracy. The coordinates

Table 1. Final coordinates of the atoms in one molecule obtained from Fourier projections.

	x	y	z
I	0.0982	0.1345	0.1005
Cl	−0.028	0.246	−0.053
N	0.205	0.033	0.248
C_1	0.270	0.126	0.330
C_2	0.126	−0.033	0.323
C_3	0.290	−0.033	0.176

Table 2. Observed and calculated structure factors. The given values are one fourth of the absolute values.

h k l	F_{obs}	F_{calc}	*h k l*	F_{obs}	F_{calc}
0 2 0	13	−13.1	4 1 0	25	−22.9
4	50	−48.7	3	33	−33.6
6	12	10.4	5	51	51.6
8	52	57.3	7	12	9.4
10	28	−32.9	9	16	−13.0
12	21	−18.7	11	<9.0	− 5.0
14	9	6.0	13	14	17.3
2 0 0	28	31.9	6 1 0	36	40.3
2	42	−43.5	3	<7.4	− 0.7
4	8	− 7.8	5	24	−23.3
6	13	−10.1	7	24	−26.5
8	24	22.5	9	20	19.1
10	14	−12.8	11	8	− 6.7
12	<8.5	3.4	8 1 0	45	49.2
14	<4.5	2.3	3	19	15.8
4 0 0	39	−40.2	5	20	−19.4
2	14	− 8.2	7	16	−15.6
4	57	60.9	9	30	34.3
6	27	−25.4	11	<6.6	− 1.7
8	22	−18.9	10 1 0	14	14.8
10	10	7.8	3	<9.6	− 5.5
12	19	17.4	5	<9.5	5.0
6 0 0	49	−50.3	7	12	− 9.1
2	<7.0	− 1.0	9	10	8.9
4	55	55.8	12 1 0	17	−14.2
6	20	−19.7	3	20	−21.3
8	26	−24.6	5	24	25.3
10	13	10.0	7	<6.4	2.7
12	15	17.1	14 1 0	9	− 6.6
8 0 0	15	14.4	3	10	−10.2
2	<8.6	− 4.1	0 0 2	21	24.7
4	13	− 9.4	4	59	−57.2
6	<9.5	1.4	6	53	−51.3
8	10	8.5	8	<7.7	1.8
10	<7.9	− 4.0	10	23	22.7
10 0 0	41	40.2	12	9	7.9
2	<9.6	1.2	2 0 2	42	45.1
4	34	−31.2	4	24	−18.7
6	15	12.9	6	27	−24.1
8	21	19.4	8	<8.0	− 3.8
10	12	−10.8	10	<8.6	5.5
12 0 0	<8.0	3.6	12	<7.1	− 5.5
2	<9.0	− 2.4	4 0 2	12	−10.0
4	18	−17.6	4	46	46.2
6	<7.3	5.1	6	29	28.5
8	<5.0	5.1	8	16	−16.8
14 0 0	13	−16.2	10	27	−31.7
2	9	8.0	12	<6.5	− 6.2
4	11	10.3	6 0 2	10	− 9.0
2 1 0	47	−55.8	4	40	41.0
3	46	−52.8	6	26	25.7
5	55	61.9	8	12	−12.6
7	14	12.0	10	22	−26.0
9	36	−33.2	12	8	− 7.1
11	<9.4	− 6.1	8 0 2	<7.7	5.3
13	20	21.7	4	11	−10.5

$h\,k\,l$	F_{obs}	F_{calc}	$h\,k\,l$	F_{obs}	F_{calc}
6	<8.6	− 3.2	8	22	−22.1
8	<9.6	− 1.7	10	32	−38.1
10	7	5.0	12	6	− 8.6
10 0 2	<8.6	6.6	0 6 2	9	− 8.9
4	26	−25.3	4	19	−17.7
6	24	−23.1	6	7	− 7.0
8	9	9.4	8	10	11.0
10	17	18.2	10	14	15.4
12 0 2	<7.9	4.4	12	7	6.3
4	10	−10.5	0 8 2	20	20.7
6	9	− 7.6	4	30	−29.1
14 0 2	10	− 9.3	6	25	−26.6
4	9	10.2	8	<8.0	0.8
1 0 2	44	−49.1	10	13	13.6
4	33	−33.1	0 10 2	12	−10.4
6	21	18.5	4	12	12.1
8	27	26.2	6	14	14.7
10	<8.6	− 2.0	8	<6.4	1.4
12	13	−12.1	0 12 2	<7.4	2.9
3 0 2	78	−82.0	4	16	15.8
4	50	−51.2	6	9	7.9
6	30	27.7	0 14 2	<3.8	3.0
8	39	36.2	0 2 1	53	−60.3
10	<8.5	− 0.9	3	69	−74.6
12	18	−18.4	5	<5.8	0.9
5 0 2	15	−13.1	7	50	51.7
4	15	−13.3	9	19	20.3
6	<7.6	− 8.0	11	16	−16.2
8	<8.5	− 1.2	13	17	−19.7
10	<8.2	1.4	0 4 1	19	12.6
12	<5.9	1.0	3	18	18.0
7 0 2	40	36.7	5	10	− 8.7
4	23	18.8	7	<7.8	− 4.6
6	31	−33.0	9	8	− 8.4
8	29	−33.6	11	7	4.5
10	<7.3	3.9	13	6	5.5
12	18	19.0	0 6 1	40	40.4
9 0 2	26	24.2	3	55	55.7
4	<8.5	0.9	5	9	− 8.7
6	15	−20.0	7	25	−24.9
8	15	−18.1	9	20	−20.3
10	<5.6	− 0.8	11	13	12.1
11 0 2	24	−20.0	0 8 1	15	−12.1
4	18	−14.1	3	20	−18.9
6	<7.3	1.3	5	8	− 5.3
8	8	6.6	7	18	18.9
13 0 2	25	−24.4	9	<7.3	2.9
4	17	−16.7	11	7	− 4.5
6	9	7.9	0 10 1	14	−17.2
0 2 2	42	−41.7	3	20	−23.0
4	8	6.7	5	<8.2	− 0.1
6	16	13.7	7	20	23.6
8	8	7.2	9	9	7.3
10	<8.5	2.8	0 12 1	10	10.1
12	7	6.9	3	14	14.1
0 4 2	13	−13.1	5	<6.2	− 4.1
4	60	60.4	7	8	−10.7
6	40	33.9	0 14 1	9	9.3

Table 3. Atomic distances and valency angles in the trimethylamine—iodo monochloride complex.

	Distance (Å)		Angle (°)
I—Cl	2.52	I—N—C_1	109
N—I	2.30	I—N—C_2	107
N—C_1	1.55	I—N—C_3	104
N—C_2	1.42	C_1—N—C_2	109
N—C_3	1.45	C_2—N—C_3	118
I—C_1	3.17	C_1—N—C_3	108
I—C_2	3.05		
I—C_3	3.00		

Table 4. N—I and I—I (resp. I—Cl) distances in addition compounds.

	N—I	I—I (I—Cl)
Pyridine · ICl	2.30	2.54
Trimethylamine · I_2	2.27	2.84
Trimethylamine · ICl	2.30	2.52

of the lighter atoms, however, are certainly less accurate. The small deviation from linearity observed for the N-I-Cl group with an angle at the I atom deviating by less than 4° from 180° may therefore not be significant. The atomic distances and bond angles derived from the coordinates listed in Table 1 are given in Table 3.

It is obvious that the type of structure found for the trimethylamine — iodo monochloride compound is closely analogous to structures previously derived for halogen addition compounds of aliphatic amines.[2] The linear arrangement nitrogen-halogen-halogen has been observed in all solid halogen addition compounds of aromatic amines so far investigated and also in the 1:1 iodine compounds of γ-picoline and quinoline which are now being investigated in this laboratory. It is interesting to note that the nitrogen-iodine bond length is very nearly the same in all these compounds, whether aliphatic or aromatic, and that the lengthening of the halogen-halogen bond as compared with the bond distance in the free iodine or iodo monochloride molecules is also practically the same (Table 4). The base property of the amine as judged from the dissociation constant in aqueous solution does not appear to be of any importance for the structure of the addition compound. The results of X-ray analyses do not substantiate Hantzsch's suggestion[3] that the solid halogen compounds of amines should be regarded as salt-like substances containing a halogen-substituted ammonium cation and a halogen anion.

Thus the evidence available from X-ray analysis of simple addition compounds formed by amines and halogens do not indicate a tendency towards the formation of ions like PyI^+. This does not mean, however, that salt-like structures cannot be formed. Some simple salts are known which must be expected to contain ions like Py_2I^+. In a recently started analysis of the crystal structure of the 1:2 compound formed by pyridine and iodine we have

actually observed the Py_2I^+ ion. According to space group requirements it has a center of symmetry. This means that the N-I-N arrangement is linear. The ion is probably at least very nearly planar. The remaining iodine atoms form an arrangement consisting of centrosymmetric I_3^- ions and iodine molecules very similar to that observed by Havinga [4] in tetra-ethylammonium heptaiodide. Additional examples of ionic compounds formed by amines and halogens will probably be found in the future.

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