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Crystal Structure of the Addition Compound 1,4-Dioxan-Chlorine

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An X-ray analysis of the 1:1 compound 1,4-dioxan chlorine carried out at temperatures between −30° and −90°C shows that the crystals are isomorphous with those of the corresponding bromine compound [1]. The monoclinic unit cell has the dimension a = 9.36 Å, b = 8.83 Å, c = 4.13 Å and β = 91.5°. The observed O—Cl and Cl—Cl distances associated with the chlorine molecule bridges are 2.67 and 2.02 Å, respectively.

During the last years a series of addition compounds formed by molecules containing a donor atom (A) and halogen molecules have been studied in the solid state by X-ray crystallographic methods. One of the most striking features observed in these compounds is the existence of linear atomic arrangements A-halogen-halogen. So far, the halogen molecules chosen have been those of iodine or bromine, in some cases also iodo monochloride. In no case have addition compounds in which chlorine is directly attached to the donor atom been studied. From our earlier experience it would in fact seem probable that a charge transfer bond between, *e.g.*, an oxygen atom and a chlorine atom should be even weaker than the bond to a bromine atom which is in turn certainly weaker than an oxygen-iodine bond.

Results, recently obtained, tend to confirm this view but show that a series of donor molecules actually form addition compounds with chlorine which are isomorphous with the bromine and even the iodine compounds. This might perhaps appear a little surprising when we consider the difference in atomic radii of the different halogen atoms. The A-halogen bond distance, however, is determined both by the size of the halogen atom and by the strength of the bond established by electron transfer between the two atoms. Although the smaller radius of the chlorine atom will tend to shorten this bond distance a certain compensation results from the fact that the bond is weaker in the case of chlorine than in the case of bromine. The analogy between crystals containing a donor molecule and chlorine and those containing the same donor molecule and bromine, even suggests the formation of »chlorine molecule bridges» in chlorine addition compounds.

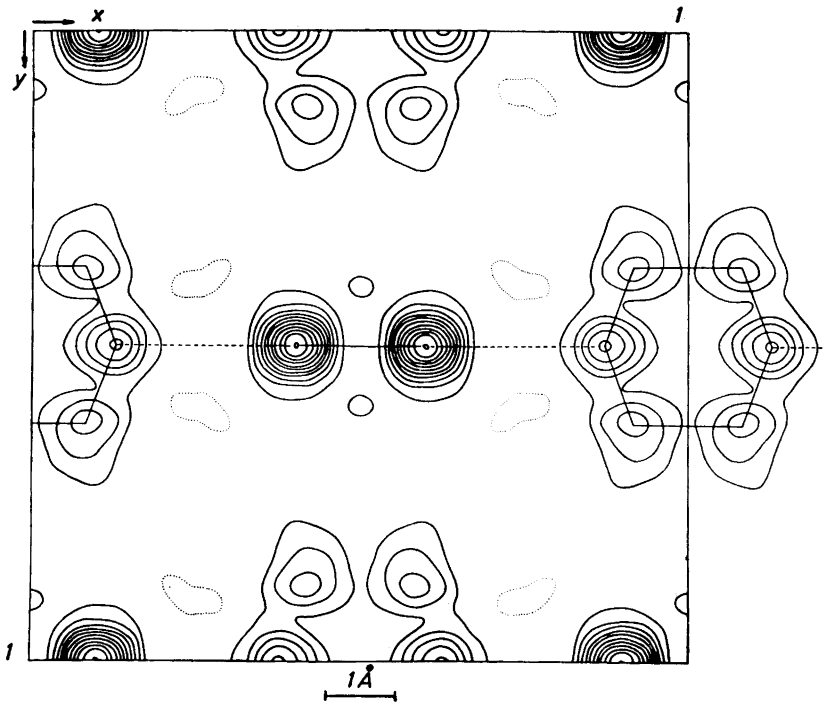

Fig. 1. Projection along [001]. Contour intervals $2\sum e$. Å^{-2}. Zero contour dotted.

Choosing first the 1:1 compound between 1,4-dioxan and chlorine, a report on the determination of the crystal structure of this compound will be given here.

Single crystals were obtained by cooling an equimolecular mixture of the two substances in a capillary tube mounted in a Weissenberg camera equipped with a cooling system. The melting point of the addition compound is approximately −5°C. Zero layer line Weissenberg photographs were taken at temperatures below −30°C, mostly at −90°C, and with rotation about the directions [001], [110] and [101] of the monoclinic cell.

The lattice parameters obtained from the diagrams are:

$$a = 9.36 \text{ Å} \qquad b = 8.83 \text{ Å} \qquad c = 4.13 \text{ Å} \qquad \beta = 91.5°$$

and the number of molecules in the unit cell *two* (density about 1.55). These figures and the following analysis confirmed the suggestion that the compound is actually isomorphous with the corresponding bromine compound and belongs to the space group $C2/m$. It was found difficult, however, to obtain good single crystals, particularily if the crystals had their c-axis approximately parallel to the axis of the capillary tube. It was observed that the crystals

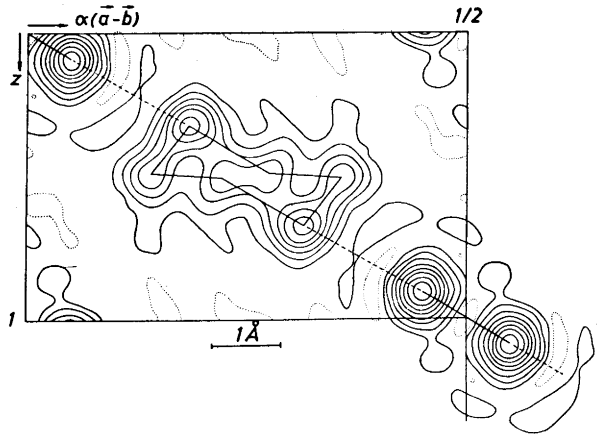

Fig. 2. Projection along [110]. Contours: 0, 2, 4, 8, 12, 16, — for chlorine and 0, 2, 4, 6, 8, 10 — for light atoms. Zero contour dotted.

have a marked tendency to grow along directions which are approximately parallel to the directions of the endless molecular chains of which the entire structure is found to be built up.

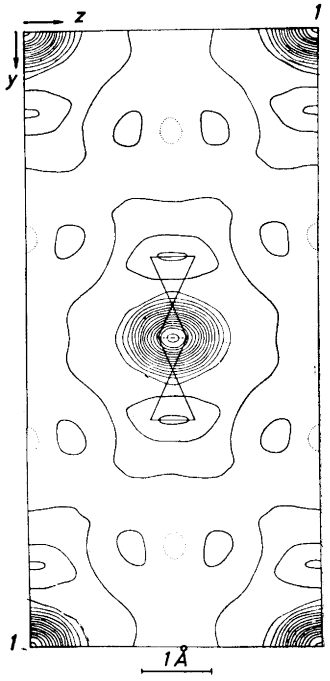

Fig. 3. Projection along [101]. Contours: 0, 2, 6, 10, 14 —. Zero contour dotted.

Table 1. Atomic coordinates in fractions of the cell-edges. Origin at a center of symmetry.

	x	*y*	*z*
O	0.371	0.000	0.322
Cl	0.101	0.000	0.094
C	0.419	0.134	0.492

Table 2. Bond distances and bond angles in the dioxan molecule.

C—C	1.52 Å (1.529);	C—O	1.44 Å (1.421)
∠ C—O—C	111° (112.5);	∠C—C—O	109° (109.0)

The suggestion that the dioxan-chlorine structure is very similar to the dioxan-bromine structure [1] made it appear reasonable to carry out the first Fourier synthesis along [001] inserting chlorine parameters almost identical with the bromine parameters found for the dioxan-bromine compound. The intensity material obtained from zero layer line photographs with rotation about the *c*-axis appeared, however, to be less satisfactory than intensity data obtained from other diagrams. For this reason the intensity material was partly supplemented by intensity data obtained from diagrams with rotation about other crystallographic directions.

The final electron density maps are reproduced in Figs. 1—3. The atomic coordinates computed using these maps are given in Table 1.

In the projection along [101] serious overlapping of atoms occurs. This is not the case in the two other projections, but the intensity material on which the [110] projection is based was considered more reliable than that leading to the [001] projection. Table 1 is mainly based on the coordinates obtained from this projection.

From the coordinates given in Table 1 the bond distances and bond angles within the dioxan molecule listed in Table 2 have been computed.

The values in parantheses are those recently obtained in this laboratory by Michael Davis from an electron diffraction study of dioxan vapour.

The Cl—Cl bond distance is 2.02 Å and thus only slightly longer than the spectroscopic value for the free molecule (1.988). The Cl—O distance obtained is 2.67 Å. The standard deviation in the Cl—Cl distance is 0.013 Å, in the *Cl*—O distance 0.026 Å and in the C—C distance 0.045 Å. It appears probable that the conclusion is legitimate that the chlorine-oxygen distance in the dioxan chlorine compound is actually slightly smaller than the bromine-oxygen distance in the corresponding bromine compound. The angle O—Cl—Cl is found equal to 178°. It appears doubtful whether or not the deviation from 180° is real. The deviation of the O—Cl bond from the direction of an equatorial bond is about 19° and in the same direction as that obtained in the bromine and iodine compounds.

The relatively small values of the temperature factor *B* ranging from 2.0 for exposures at the lowest temperature to 2.8 for the high temperature, indicate a relatively rigid structure.

Table 3. Observed and calculated structure factors. The figures represent one half of the absolute values.

h k l	*F*obs	*F*calc	*h k l*	*F*obs	*F*calc
	(*h h l*) zone				
1 1 4	11.9	−13.1			
1 1 0	1.4	1.7	2 2 4	5.4	− 5.2
2 2 0	6.1	5.1	3 3 4	6.2	− 5.9
3 3 0	1.0	1.2	4 4 4	3.4	3.6
4 4 0	15.7	−15.5	5 5 4	3.7	4.2
5 5 0	12.7	−11.9	1 1 $\bar{4}$	<1.4	− 0.3
6 6 0	10.1	− 9.0	2 2 $\bar{4}$	<1.4	1.0
7 7 0	<1.3	− 1.0	3 3 $\bar{4}$	7.6	9.3
8 8 0	2.2	1.5	4 4 $\bar{4}$	7.3	8.9
0 0 1	3.9	− 2.1	5 5 $\bar{4}$	1.8	1.6
1 1 1	16.1	13.6	0 0 5	8.0	−11.1
2 2 1	4.0	4.4	1 1 5	2.0	− 2.4
3 3 1	22.0	−20.3			
4 4 1	16.1	−15.5	2 2 5	2.6	− 3.8
5 5 1	6.2	− 5.2	1 1 5	2.5	− 2.3
6 6 1	5.9	− 4.4	2 2 5	0.8	0.8
7 7 1	<1.2	1.4	3 3 5	0.5	0.5
8 8 1	4.6	4.9			
1 1 $\bar{1}$	44.3	47.3		(*h k* $\bar{h}$) zone	
2 2 $\bar{1}$	10.2	7.6	0 2 0	37.1	38.1
3 3 $\bar{1}$	6.6	5.5	0 4 0	19.1	16.4
4 4 $\bar{1}$	4.8	− 5.1	0 6 0	23.3	19.5
5 5 $\bar{1}$	12.6	−12.1	0 8 0	15.2	15.1
6 6 $\bar{1}$	7.0	− 5.5	0 10 0	6.1	5.5
7 7 $\bar{1}$	9.5	− 9.3	1 1 $\bar{1}$	41.9	42.1
8 8 $\bar{1}$	<0.7	− 0.7	1 3 $\bar{1}$	19.3	19.1
0 0 2	10.9	12.8	1 5 $\bar{1}$	17.9	16.0
1 1 2	1.3	− 1.1	1 7 $\bar{1}$	17.1	17.5
2 2 2	17.3	−18.1	1 9 $\bar{1}$	10.0	8.9
3 3 2	14.2	−13.9	1 11 $\bar{1}$	2.8	3.3
4 4 2	6.2	− 3.8	2 0 $\bar{2}$	25.8	28.3
5 5 2	10.6	− 9.0	2 2 $\bar{2}$	18.3	19.9
6 6 2	3.1	2.7	2 4 $\bar{2}$	12.4	12.4
7 7 $\bar{2}$	7.9	9.0	2 6 $\bar{2}$	11.9	12.6
1 1 $\bar{2}$	6.7	7.6	2 8 $\bar{2}$	9.7	9.6
2 2 $\bar{2}$	18.9	21.5	2 10 $\bar{2}$	3.4	4.3
3 3 $\bar{2}$	6.2	5.7	3 1 $\bar{3}$	12.0	13.3
4 4 $\bar{2}$	6.1	7.2	3 3 $\bar{3}$	8.6	10.4
5 5 $\bar{2}$	5.0	− 5.2	3 5 $\bar{3}$	8.1	8.9
6 6 $\bar{2}$	11.2	−11.2	3 7 $\bar{3}$	6.7	6.9
7 7 $\bar{2}$	3.3	− 2.0	4 0 $\bar{4}$	3.7	6.2
0 0 3	3.0	− 4.2	4 2 4	5.3	6.7
1 1 3	9.8	− 8.6	4 4 4	4.6	6.3
2 2 3	12.6	−12.8	4 6 4	<1.9	4.2
3 3 3	5.9	− 5.5			
4 4 3	9.7	− 9.2		(*h k* 0) zone	
5 5 3	4.4	4.6	2 0 0	17.8	17.7
6 6 $\bar{3}$	6.9	6.9	4 0 0	31.4	−31.4
1 1 $\bar{3}$	5.3	4.7	6 0 0	16.0	−16.1
2 2 $\bar{3}$	11.1	11.9	8 0 0	4.1	3.6
3 3 $\bar{3}$	10.9	12.5	1 1 0	1.2	1.6
4 4 $\bar{3}$	2.2	2.4	3 1 0	<1.8	0.6
5 5 $\bar{3}$	5.0	4.9	5 1 0	6.2	− 4.0
6 6 $\bar{3}$	3.9	− 2.2	7 1 0	3.4	− 2.9
0 0 4	3.7	− 3.1	0 2 0	38.2	38.7

h k l	*F*obs (*h k* 0) zone	*F*calc	*h k l*	*F*obs	*F*calc
			4 6 0	10.5	−11.6
2 2 0	5.3	5.5	6 6 0	9.0	− 6.9
4 2 0	19.6	−21.7	8 6 0	<2.9	2.9
6 2 0	7.9	− 8.0	1 7 0	<3.1	1.5
8 2 0	4.1	5.9	3 7 0	<3.2	− 0.6
1 3 0	21.7	19.8	5 7 0	3.5	− 3.1
3 3 0	0.9	1.1	7 7 0	<2.8	− 0.6
5 3 0	14.9	−15.0	0 8 0	12.8	14.0
7 3 0	7.9	− 8.5	2 8 0	3.8	3.8
0 4 0	16.1	15.8	4 8 0	7.8	− 8.6
2 4 0	<2.3	− 0.6	6 8 0	6.7	− 6.4
4 4 0	13.9	−13.5	8 8 0	1.9	1.3
6 4 0	3.1	− 2.4	1 9 0	<3.1	2.7
8 4 0	4.4	6.5	3 9 0	<2.8	− 0.7
1 5 0	10.6	11.1	5 9 0	<2.5	− 3.4
3 5 0	<2.8	0.2	7 9 0	<1.5	− 1.2
5 5 0	11.2	− 9.8	0 10 0	5.1	5.0
7 5 0	4.5	− 5.8	2 10 0	<2.5	0.7
0 6 0	19.7	18.8	4 10 0	3.7	− 4.2
2 6 0	3.0	3.9			

The reliability factors of the final projections are as follows: [001], R=8.0%; [110], R = 11.6 %; [101], R = 9.0 %.

In Table 3 calculated and observed structure factors are listed. The number of reflexions available for the [001], [110] and [101] projections are 34, 64, and 24, respectively (maximum with CuK-radiation 60, 69, and 26). f-Values given by Berghuis *et al.*[2] were used for carbon and oxygen, for chlorine the values given in *Int. Tab.*[3].

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