

Crystal Structures of Oxalyl Bromide and Oxalyl Chloride

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Details are presented of crystal structure determinations of oxalyl bromide and oxalyl chloride. The crystals are not isomorphous and their structures quite different. In the oxalyl bromide structure weak charge transfer bonds connect every molecule with its four nearest neighbours, the O...Br separation (3.27 Å) being only slightly shorter than the expected van der Waals separation. The C—Br...O angle is found equal to 169°.

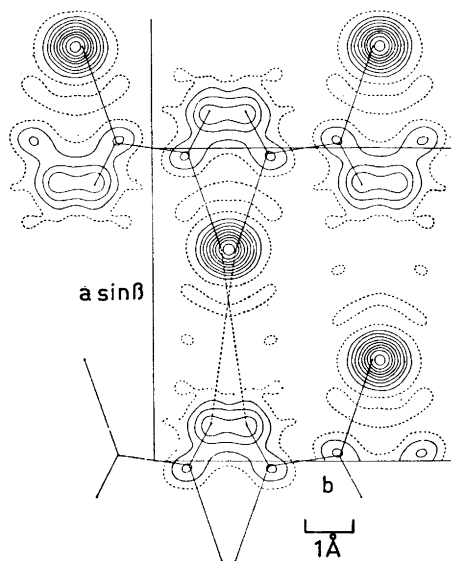
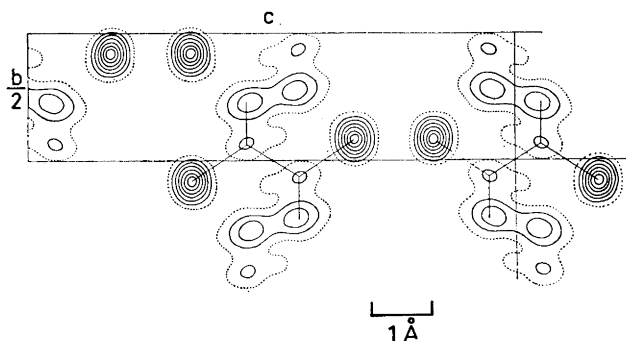
In the oxalyl chloride structure charge transfer bonds between oxygen and chlorine are not indicated.

In order to collect empirical facts regarding the atomic arrangement in solids containing charge transfer bonds the crystal structure of a considerable number of addition compounds formed by typical donor molecules and halogen molecules have been determined and general principles formulated¹. As had already been suggested² the bonds mainly responsible for the formation of the 1:3 addition compounds between iodoform and quinoline or sulphur (S₈) and the corresponding sulphur compound of antimony triiodide are in fact iodine-nitrogen resp. iodine-sulphur bonds. This has been proved by crystal structure determinations carried out in our laboratory during the last few years³. Moreover, the arrangement carbon-iodine-donor atom (resp. antimony-iodine-sulphur) is very nearly *linear* in all cases and corresponds to the arrangement halogen-halogen-donor atom observed in all true addition compounds in which a halogen molecule is the acceptor. In the 1:1 addition compound 1,4-dithiane-iodoform the same type of iodine-sulphur bonds have also been observed⁴. Similar but obviously much weaker bonds have been found in two 1:1 addition compounds formed by 1,4-dioxan and oxalyl halides⁵.

The question now arose if intermolecular charge transfer bonds might not be expected even in crystals containing a single molecular species when the molecule in question contains both electron donor and electron acceptor atoms. In the crystalline cyanogen halides infinite linear chains of molecules have been observed which indicate the presence of comparatively strong bonds connecting nitrogen belonging to one molecule and halogen belonging to the neighbour molecule. In the trimeric forms — the cyanuric halides — analogous bonds might be expected to occur between tertiary nitrogen atoms and halogen

Table 1. Lattice parameters, space groups for oxalyl bromide (A) and oxalyl chloride (B).

	A	B
<i>a</i>	6.18 Å	6.44 Å
<i>b</i>	5.46 Å	6.08 Å
<i>c</i>	7.80 Å	11.93 Å
β	112.4°	
Space group	$P2_1/c$	$Pbca$
<i>Z</i>	2	4

Fig. 1 a. Fourier projection of oxalyl bromide along [001]. Contour lines at intervals of $3 \text{ e.}\text{\AA}^{-2}$ for C and O, $12 \text{ e.}\text{\AA}^{-2}$ for Br. Dotted line corresponds to $3 \text{ e.}\text{\AA}^{-2}$.Fig. 1 b. Fourier projection of oxalyl chloride along [100]. Contour lines at intervals of $3 \text{ e.}\text{\AA}^{-2}$. Dotted line corresponds to $3 \text{ e.}\text{\AA}^{-2}$.

atoms, leading to infinite planar nets. The results of a preliminary X-ray investigation appeared to confirm this suggestion⁶ although the authors seem to have overlooked the possibility of the bonds just mentioned.

In crystals of certain carboxylic acid halides the possibility of charge transfer bonds between halogen and oxygen appeared to be possible. As a consequence of the observations made in the case of the crystalline addition compounds formed by oxalyl chloride and oxalyl bromide with dioxan we started X-ray work on the oxalyl halides themselves. These two substances are not isomorphous as might perhaps have been expected, had the melting point of the chloride not been higher than that of the bromide (-12°C and -19.5°C , respectively). However, the space group symmetry and the number of molecules in the unit cells (*cf.* Table 1) require the molecules to be crystallographically equivalent and centrosymmetrical in both cases. The crystallographic findings therefore indicate that if charge transfer bonds exist at all, every molecule must take part in the formation of *four* such bonds.

The X-ray analysis of the two substances, which are both liquid at room temperature, had to be carried out at a lower temperature and the single crystals were grown in capillary tubes. Prolonged trials revealed that it is indeed possible to obtain crystals in which one of the crystallographic directions is approximately parallel to the axis of the capillary tube, and it was found that this direction is not necessarily always the same. Weissenberg single crystal technique could therefore conveniently be employed both for the chloride and the bromide and two-dimensional Patterson and Fourier syntheses worked out. The atomic coordinates thus arrived at were then refined using least squares computations. The axes of rotation were [010], [100] and [110] in the case of the chloride, [010], [001] and [011] in the case of the bromide. Final atomic parameters are listed in Table 2. Structure factors (F_c) computed from these coordinates together with the observed values (F_o) may be found in Table 3. In Figs. 1a and b one electron density map is reproduced for each of the two substances. For the bromine compound a second Fourier map has previously been published⁷.

The results obtained for the bromide confirm the suggestion that charge transfer bonds are present between neighbouring molecules. The oxalyl bromide structure may indeed be described as being built up of (non-planar) sheets within which every molecule is linked to four neighbours by O...Br bonds of length 3.27 Å a value only slightly smaller than that expected for a van der Waals contact. The angle C—Br..O is 169° . Moreover, it follows from the atomic coordinates given in Table 2 that the oxalyl bromide molecules are at least very nearly planar with bond distances and angles listed in Table 4. Within the sheet an intermolecular O—Br separation of 3.63 Å is also observed;

Table 2. Final atomic coordinates for oxalyl bromide (A) and oxalyl chloride (B).

	A				B		
	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
Br	0.321	0.228	0.162	Cl	-0.084	-0.083	0.167
O	0.883	0.191	0.377	O	0.118	0.230	0.050
C	0.020	0.119	0.906	C	-0.006	0.062	0.053

Table 3.

a. Observed calculated structure factors for oxalyl bromide.

hk0-projection											
<i>h</i>	<i>k</i>	F_o	F_c	<i>h</i>	<i>k</i>	F_o	F_c	<i>h</i>	<i>k</i>	F_o	F_c
0	1	11	-13	2	2	50	49	4	4	10	-9
0	2	49	-49	2	3	59	-55	4	5	19	-20
0	3	73	76	2	4	17	16	4	6	10	13
0	4	17	-15	2	5	32	33	5	1	28	-28
0	5	35	-36	2	6	22	-23	5	2	20	21
0	6	28	29	3	1	60	55	5	3	5	5
1	1	85	-90	3	2	55	-51	5	4	19	-19
1	2	90	91	3	3	17	-15	5	5	9	10
1	3	29	26	3	4	35	36	6	0	19	-18
1	4	55	-55	3	5	20	-18	6	1	9	9
1	5	22	21	3	6	10	-10	6	2	10	10
1	6	9	10	4	0	40	42	6	3	15	-16
1	7	19	-24	4	1	25	-24	7	1	8	11
2	0	115	-112	4	2	32	-31				
2	1	30	29	4	3	31	30			$R = 5.1\%$	

h0l-projection											
<i>h</i>	<i>l</i>	F_o	F_c	<i>h</i>	<i>l</i>	F_o	F_c	<i>h</i>	<i>l</i>	F_o	F_c
0	1	31	28	2	0	23	-24	4	2	11	-10
0	2	17	-15	2	1	13	12	5	4	9	12
0	3	28	-21	2	2	36	30	5	3	9	10
0	4	12	-10	2	3	12	10	5	1	17	-21
1	4	11	-9	2	4	2	-2	5	0	17	-18
1	3	19	15	3	4	8	-7	5	1	6	4
1	2	40	36	3	3	24	-25	5	2	9	10
1	1	38	36	3	2	22	-27	6	3	12	-16
1	0	5	-7	3	1	18	22	6	2	11	-13
1	1	61	-52	3	0	34	38	6	0	13	13
1	2	17	-14	3	1	25	23	6	1	11	11
1	3	9	7	3	3	18	-12	7	2	8	11
1	4	10	10	4	4	10	-9	7	1	7	9
2	4	14	14	4	2	18	24				
2	3	18	15	4	1	21	27				
2	2	23	-23	4	0	8	-8				
2	1	39	-41	4	1	20	-18			$R = 14.1\%$	

Projection along [011]. $h' = h; k' = k-l; l' = l = 0.$											
<i>h</i>	<i>k'</i>	F_o	F_c	<i>h</i>	<i>k'</i>	F_o	F_c	<i>h</i>	<i>k'</i>	F_o	F_c
0	1	20	-27	2	2	67	76	4	2	36	-41
0	2	32	-38	2	1	20	-13	4	0	20	-16
0	3	9	-11	2	0	50	-48	4	2	39	39
0	4	23	-19	2	1	7	-3	4	4	10	-17
1	4	39	-41	2	2	15	-12	5	2	44	-43
1	3	9	-5	2	3	11	12	5	0	38	36
1	2	40	45	2	4	26	27	5	1	9	7
1	1	31	26	3	4	23	23	5	3	8	-8
1	0	12	13	3	2	27	28	6	4	13	-18
1	1	8	2	3	1	17	14	6	0	31	31
1	2	81	-89	3	0	76	-77	6	2	18	-20
1	4	25	27	3	2	42	34	7	2	15	17
2	4	18	-19	3	4	7	6				
2	3	10	-10	4	4	30	33			$R = 12.3\%$	

b. observed and calculated structure factors for oxalyl chloride.

h0l-projection								
<i>h l</i>	F_o	F_c	<i>h l</i>	F_o	F_c	<i>h l</i>	F_o	F_c
0 1	8	- 9	2 4	7	- 6	5 1	7	7
0 2	12	- 11	2 5	3	4	5 2	4	3
0 3	24	- 23	2 6	4	3	5 3	3	1
0 4	17	- 17	2 7	1	1	5 4	3	- 3
0 5	9	10	3 1	20	20	5 5	2	- 2
0 6	8	6	3 2	28	27	5 6	1	0
0 7	3	3	3 3	3	- 4	6 0	9	- 9
1 1	13	14	3 4	10	- 10	6 1	5	- 5
1 2	28	28	3 5	7	- 8	6 2	3	4
1 3	6	- 7	3 6	1	0	6 3	6	7
1 4	7	- 5	3 7	2	3	6 4	1	2
1 5	4	- 6	4 0	16	- 15	6 5	1	- 2
1 7	2	2	4 2	4	3	7 1	2	- 2
2 0	36	37	4 3	5	7			
2 1	3	0	4 4	2	4			
2 2	5	- 5	4 5	2	- 2			
2 3	11	- 9	4 6	2	- 2			

$R = 10.2\%$

0kl-projection								
<i>k l</i>	F_o	F_c	<i>k l</i>	F_o	F_c	<i>k l</i>	F_o	F_c
0 2	10	8	1 7	17	14	2 7	10	11
0 4	14	- 12	1 8	5	- 3	2 8	2	2
0 6	27	24	1 9	2	- 2	2 11	4	- 5
0 8	19	- 21	1 10	2	- 1	2 12	3	- 3
0 10	11	- 11	1 11	7	- 7	2 13	4	3
0 12	9	8	1 12	5	5	3 0	11	- 12
0 14	3	- 4	1 13	7	6	3 3	5	- 1
1 0	9	12	1 14	2	- 2	3 5	3	- 1
1 1	24	29	2 0	4	- 6	3 6	7	- 7
1 2	18	- 18	2 1	16	17	3 8	4	4
1 3	8	- 10	2 2	10	10			
1 4	9	- 10	2 4	6	6			
1 5	28	- 28	2 5	12	- 13			
1 6	16	15	2 6	9	- 9			

$R = 12.6\%$

Projection along [100]. $h' = h - k$; $k' = h + k = 0$; $l' = l$.

<i>h' l</i>	F_o	F_c	<i>k l</i>	F_o	F_c	<i>k l</i>	F_o	F_o
0 2	17	16	1 13	3	3	3 7	5	- 4
0 4	24	- 23	1 14	5	- 5	3 8	4	2
0 6	48	46	1 15	3	- 6	3 10	2	0
0 8	34	- 37	2 0	31	32	3 12	3	- 1
0 10	19	- 21	2 1	29	- 25	4 0	3	3
0 12	17	15	2 3	5	2	4 1	14	10
0 14	5	- 7	2 5	20	20	4 2	7	- 5
1 1	67	72	2 6	6	10	4 3	9	3
1 2	17	- 15	2 7	15	- 14	4 4	6	- 3
1 3	49	- 47	2 8	8	- 7	4 6	4	5
1 4	53	55	2 10	4	- 3	4 7	7	7
1 5	29	26	2 11	4	8	5 1	3	5
1 6	14	14	2 13	6	- 4	5 2	4	4
1 7	11	12	3 1	10	8	5 3	5	- 9
1 8	13	- 11	3 2	10	7	5 4	4	- 4
1 9	26	- 25	3 3	7	6	5 5	4	4
1 10	8	11	3 4	12	10	5 7	2	3
1 11	9	8	3 5	4	- 1			
1 12	3	- 2	3 6	6	6			

$R = 14.1\%$

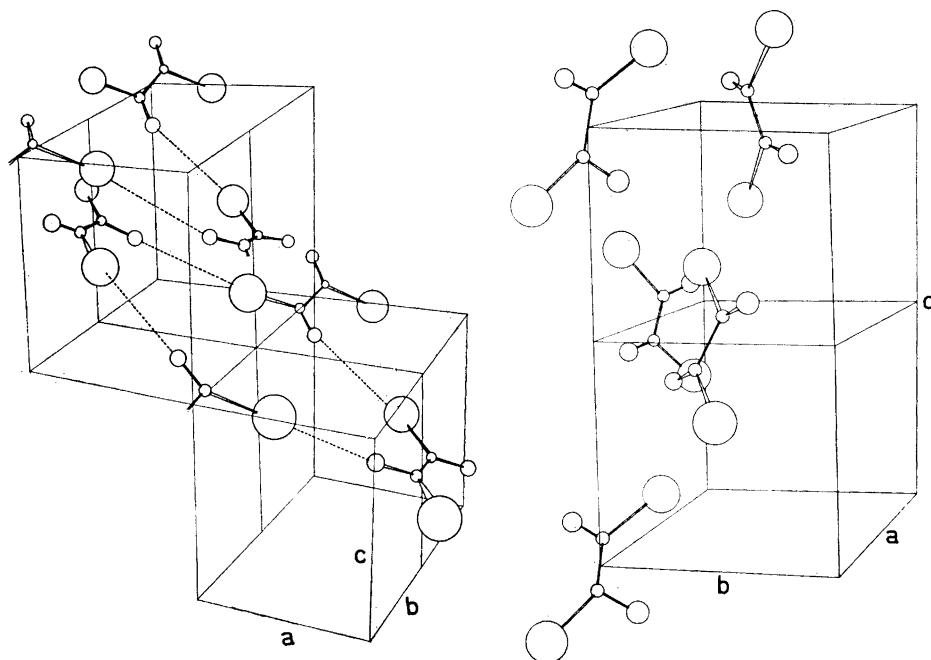


Fig. 2 a. Drawing of the oxalyl bromide structure.

Fig. 2 b. Drawing of the oxalyl chloride structure.

the nearest approach between O and Br atoms belonging to neighbouring sheets is still larger, *viz.* 3.90 Å. Fig. 2a visualizes both the arrangement within the sheets and the mutual arrangement of neighbouring sheets.

The structure of oxalyl chloride differs very much from that of the bromide, although the molecules are situated in centres of symmetry even in this case. The shortest O—Cl separation is found equal to 3.50 Å and the angle C—O...Cl is very far from approaching 180°. It must therefore be admitted that in the oxalyl chloride structure no indications of bonds connecting chlorine and oxygen atoms can be traced. The oxalyl chloride structure is reproduced schematically in Fig. 2b. Unlike the oxalyl bromide molecules the molecules of oxalyl chloride do not appear to be strictly planar. The aim of the present investigation was not, however, to arrive at a very accurate determination of the parameters of the latter molecule. The computed values for the oxalyl chloride molecule probably being less reliable than those listed for the bromide molecule — the former are not included in Table 4.

Table 4. Bond distances and bond angles within the oxalyl bromide molecule.

Distance		Angle	
O—Br	1.84 Å	O—C—Br	128.3°
C=O	1.17 Å	Br—O—C	108.8°
C—C	1.56 Å	O—C—C	122.3°

It would appear interesting to investigate crystal structures of substances containing electron donors like, *e.g.*, oxygen and as acceptors halogen atoms directly linked not to carbon but rather to atoms known to be more strongly electronegative, for example nitrogen. In such crystals one might expect the formation of somewhat stronger bonds between halogen and the donor atom. One structure of this kind has accidentally been investigated, namely that of N-chlorosuccinimide⁸. Here, the arrangement N—Cl...O is nearly linear (the N—Cl—O— angle being approximately 170°) and the Cl—O distance (2.88 Å) is significantly shorter than the van der Waals radius sum. Addition compounds might be expected to exist between N-halogenosuccinimide and a number of molecules containing donor atoms. So far, we have not been able to prepare crystals of such compounds, however, probably because of the high chemical reactivity of the halogen atom in N-halogenosuccinimides.

This investigation has in part been sponsored by the *United States Air Force Development Command* under the contract AF 61 (052)—71.

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Received June 21, 1962.