

References

- CROMER, D. T. & OLSEN, C. E. (1959). *Acta Cryst.* **12**, 689.
Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935). Berlin: Borntraeger.

- SANDS, D. E., ZALKIN, A. & KRIKORIAN, O. H. (1959). *Acta Cryst.* **12**, 461.
 VIERVOLL, H. & ØGRIM, O. (1949). *Acta Cryst.* **2**, 277.
 VOGEL, R. (1947). *Metallforschung*, **2**, 97.

Acta Cryst. (1959). **12**, 859

The Crystal Structure of ISbCl_8 and IAICl_6

BY C. G. VONK AND E. H. WIEBENGA

Laboratorium voor Anorganische en Fysische Chemie der Rijksuniversiteit, Groningen, The Netherlands

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ISbCl_8 crystallizes in the space group $P4_1$, with four units ISbCl_8 per cell. The coordinates of the Sb and I atoms were found from the [010] Patterson synthesis. Approximate coordinates of the chlorine atoms were obtained by the heavy-atom technique. The coordinates were refined by successive Fourier-syntheses of the [010] projection. The structure consists of ICl_2^+ and SbCl_6^- ions, which are linked to chains by weak covalent bonds.

IAICl_6 crystallizes in the space group $P2_1$ with two units IAICl_6 per cell. The positions of the I atoms were found from Patterson syntheses of the main projections. The positions of the Cl atoms were again determined by the heavy-atom method. This structure consists of chains in which ICl_2^+ and AlCl_4^- ions alternate.

Introduction

Some interhalogen compounds react with metal chlorides to give ionic addition compounds. In the more familiar type of these compounds the interhalogen molecule is used in the formation of a negative ion, e.g. ICl_2^- , IBrCl^- , ICl_4^- , BrF_4^- , etc. Emeléus and his coworkers have shown that also complex positive ions (BrF_2^+ , IF_4^+) can be derived from some of the interhalogens. Electrochemical experiments indicate for instance the existence of BrF_2^+ ions in BrSbF_8 (Woolf & Emeléus, 1949).

We found that ICl_3 reacts quite readily with SbCl_5 and AlCl_3 to give the compounds ISbCl_8 and IAICl_6 respectively (Vonk, 1959). In view of the analogy between the formulae of BrSbF_8 and ISbCl_8 it seemed obvious to assume that ISbCl_8 is built up of ICl_2^+ and SbCl_6^- ions. Some electrochemical experiments, in which POCl_3 and liquid SO_2 were used as solvents, were undertaken to verify this assumption. These experiments however failed because ISbCl_8 decomposes in both solvents. It was therefore decided to determine the structures of both ISbCl_8 and IAICl_6 by X-ray diffraction.

 ISbCl_8

This compound is obtained as red needle-like crystals when a hot solution of ICl_3 in SbCl_5 is allowed to cool to room temperature. It is also formed when Cl_2 gas is passed through a solution of ICl in SbCl_5 .

ISbCl_8 is rapidly attacked by moist air, while on

heating it decomposes at about 60 °C. into SbCl_5 , ICl and Cl_2 . During the X-ray exposures the crystals were kept in thin-walled pyrex tubes.

The photographs showed tetragonal symmetry.

Unit cell:

$$a=b=6.98 \pm 0.03, \quad c=24.2 \pm 0.1 \text{ \AA}.$$

Reflections $00l$ absent for $l \neq 4n$. Space group $P4_1$. Density, calculated from the unit-cell volume, assuming 4 ISbCl_8 units per cell: 3.00 g.cm.⁻³. Observed density 3.0(±0.2) g.cm.⁻³. Crystal habit: Rapidly grown crystals are needle-like along [001] and show the forms {100}, {001} and {101}. Slowly grown crystals may also show the forms {102}, {103} and {104}.

Intensities

The intensities of 68 reflections $hk0$ and 161 reflections $h0l$ were obtained from integrated and non-integrated Weissenberg photographs taken with Zr-filtered Mo-radiation.

The dimensions of the crystal used for the determination of the intensities $h0l$ were: 0.06 (rotation axis) × 0.06 × 0.16 mm. Because of the relatively large dimensions of the cross section perpendicular to the rotation axis and the relatively large linear absorption coefficient $\mu=70 \text{ cm.}^{-1}$, a correction for absorption was applied. For the reflections $hk0$ the absorption correction was neglected, since these reflections were obtained from a crystal with a cross section of $0.04 \times 0.04 \text{ mm.}^2$ perpendicular to the rotation axis.

THE CRYSTAL STRUCTURE OF ISbCl_3 AND IAlCl_6 Table 1. *Experimental and calculated structure factors for ISbCl_3*

hOl	$ F_o $	$ F_c $	α	hOl	$ F_o $	$ F_c $	α	hOl	$ F_o $	$ F_c $	α
100	163	176	0	308	26	27	79	4,0,17	< 28	3	57
200	168	168	180	408	81	87	346	5,0,17	57	55	165
300	72	64	180	508	57	48	358	6,0,17	35	35	113
400	172	175	0	608	33	37	355				
500	107	97	0	708	44	45	3	1,0,18	59	68	228
600	61	52	180	808	81	98	358	2,0,18	81	80	203
700	35	32	0					3,0,18	37	30	157
800	63	70	0	109	< 18	16	250	4,0,18	76	66	85
				209	55	61	322	5,0,18	< 34	30	184
101	33	35	295	309	48	34	352	6,0,18	72	74	221
201	30	29	346	409	68	56	156	7,0,18	41	46	197
301	85	74	344	509	83	84	146				
401	28	28	165	609	39	34	177	1,0,19	118	125	95
501	89	88	160					2,0,19	30	37	109
601	55	54	115	1,0,10	59	54	190	3,0,19	46	35	338
701	50	43	322	2,0,10	166	164	192	4,0,19	35	30	308
				3,0,10	100	110	139	5,0,19	59	59	143
102	113	108	210	4,0,10	80	90	90				
202	150	151	206	5,0,10	< 12	10	176	0,0,20	< 28	28	44
302	100	96	126	6,0,10	107	118	214	1,0,20	30	40	325
402	111	117	81	7,0,10	66	68	224	2,0,20	70	71	340
502	42	40	159					3,0,20	63	56	342
602	120	117	24C	1,0,11	126	124	107	4,0,20	50	52	20
702	80	78	204	2,0,11	131	129	48	5,0,20	39	30	36
				3,0,11	107	113	305				
103	185	229	83	4,0,11	50	50	229	1,0,21	79	71	98
203	63	58	218	5,0,11	63	58	170	2,0,21	61	58	146
303	131	125	298	6,0,11	26	22	49	3,0,21	78	78	259
403	78	74	259	7,0,11	57	54	350	4,0,21	46	41	318
503	107	105	140					5,0,21	39	37	21
603	74	63	186	0,0,12	87	72	154				
703	72	66	289	1,0,12	33	37	107	1,0,22	52	50	180
803	39	42	39	2,0,12	50	43	18	2,0,22	32	40	158
				3,0,12	106	112	357	3,0,22	57	60	211
004	56	42	11	4,0,12	89	89	352	4,0,22	57	53	266
104	70	64	0	5,0,12	62	72	338				
204	144	145	338	6,0,12	30	27	59	1,0,23	33	27	312
304	127	122	0					2,0,23	44	36	242
404	100	96	2	1,0,13	146	149	95	3,0,23	44	39	233
504	63	57	40	2,0,13	< 23	16	6	4,0,23	< 32	26	89
604	61	48	276	3,0,13	74	74	234	5,0,23	35	32	39
704	< 12	14	2	4,0,13	22	31	280				
804	40	34	64	5,0,13	96	96	59	0,0,24	87	74	324
				6,0,13	39	33	345	1,0,24	72	69	346
105	174	196	91	7,0,13	55	56	243	2,0,24	< 32	19	33
205	203	222	135					3,0,24	33	16	107
305	133	133	235	1,0,14	42	35	104	4,0,24	39	37	347
405	55	42	303	2,0,14	124	130	160				
505	65	67	11	3,0,14	76	78	222	1,0,25	< 32	17	295
605	39	31	129	4,0,14	68	80	241	2,0,25	< 32	41	324
705	63	60	217	5,0,14	35	39	195	3,0,25	< 32	18	319
				6,0,14	83	84	119	4,0,25	< 32	32	197
106	112	113	145	7,0,14	44	48	154				
206	144	140	161					1,0,26	37	35	182
306	118	108	198	1,0,15	28	27	35	2,0,26	65	60	195
406	112	110	268	2,0,15	< 23	7	117	3,0,26	35	36	134
506	< 17	8	136	3,0,15	52	48	173	4,0,26	35	38	45
606	94	104	147	4,0,15	< 28	41	22				
706	59	57	127	5,0,15	85	87	41	1,0,27	35	32	123
				6,0,15	39	48	56	2,0,27	33	37	37
107	78	76	285					3,0,27	57	53	304
207	135	132	236	0,0,16	290	329	0				
307	96	96	230	1,0,16	70	59	345	0,0,28	37	52	16
407	24	13	95	2,0,16	120	124	174	1,0,29	54	46	101
507	79	79	40	3,0,16	< 29	28	190	0,0,32	89	82	0
607	< 28	17	64	4,0,16	116	110	8				
707	37	38	193	5,0,16	74	88	358				
008	26	28	265	1,0,17	33	34	297				
108	133	136	9	2,0,17	57	47	340				
208	40	41	164	3,0,17	33	43	347				

Table 1 (cont.)

<i>hk0</i>	$ F_o $	F_c	<i>hk0</i>	$ F_o $	F_c	<i>hk0</i>	$ F_o $	F_c	<i>hk0</i>	$ F_o $	F_c
100	166	176	220	81	-71	440	18	4	710	35	39
200	166	-168	230	122	-108	450	61	43	720	70	-74
300	56	-64	240	26	-10	460	24	21	730	22	-13
400	168	175	250	50	-58	470	85	89	740	24	25
500	89	97	260	69	-73	480	35	32	750	< 12	-10
600	52	-52	270	131	-139	510	54	-58	760	44	-60
700	30	32	280	43	-42	520	91	-87	770	26	-28
800	61	70	310	41	39	530	52	47	780	28	33
900	30	19	320	44	49	540	76	72	810	98	96
10,0,0	30	-31	330	67	-63	550	52	39	820	< 12	3
110	28	26	340	61	-65	560	< 10	0	830	31	-24
120	135	-136	350	< 10	-7	570	28	19	840	31	25
130	118	-112	360	28	-24	610	85	-88	850	65	52
140	48	48	370	22	-14	620	57	-66	860	< 12	10
150	85	79	380	28	19	630	44	50	870	< 12	-2
160	26	-20	390	43	44	640	59	68	880	31	30
170	67	-60	410	137	127	650	41	-44	950	39	45
210	26	17	420	18	28	660	91	-99	10,1,0	35	-34
			430	30	37	670	33	-40			

Determination of the structure

Because of the tetragonal symmetry the positions of the heavy atoms could be obtained from one, [010], Patterson synthesis, especially from the Harker maxima at $z = \frac{1}{4}$ and $z = \frac{3}{4}$. Because of the small difference in atomic number, no distinction could be made between Sb and I.

To find the x - and y -coordinates of the Cl atoms Fourier syntheses of the centrosymmetric [001] projection were computed. In the first of these syntheses the signs of 47 structure factors could be determined with reasonable certainty from the contribution of the heavy atoms. After the third synthesis further refinement of this projection was practically impossible because of overlap. Of the eight independent Cl atoms seven could be located.

Next a Fourier synthesis of the non-centrosymmetric [010] projection was prepared. Approximate values of the phase angles of the structure factors were calculated from the positions of the heavy atoms. About half of the available structure amplitudes were not used for this synthesis because the calculated phase angles were too uncertain.

As was to be expected the resulting synthesis showed, apart from the high maxima due to the heavy atoms, twice as many low maxima as Cl atoms to be located. With the aid of the x - and y -coordinates from the [001] Fourier synthesis, most of these maxima could be divided into 'real' and 'false' ones. It was found that one half of the heavy atoms was octahedrally surrounded by six Cl atoms. These units were assumed to be SbCl_6^- ions. Furthermore approximately rectangular units ICl_2^+ could be distinguished.

Refinement of the coordinates

First the [010] projection was refined by means of four successive Fourier and $(F_o - F_c)$ syntheses; the coordinates were changed according to the double-

shift rule. The shifts in the z -direction for atoms related by the tetragonal screw axis were averaged. For the heavy atoms an anisotropic temperature factor of the form

$$\exp \{ -[B_{xy} + (B_z - B_{xy}) \cos^2 \varphi] \sin^2 \theta / \lambda^2 \}$$

was introduced in the last stage of the refinement. In this expression φ is the angle between the normal of the reflecting plane and the z -axis. Values for B_{xy} and B_z were obtained by comparing F_o and F_c in two groups of reflections $h0l$ with values of $\cos^2 \varphi$ between 0 and $\frac{1}{4}$, and between $\frac{3}{4}$ and 1 respectively; only reflections with a relatively small contribution of the Cl atoms were used. A separate isotropic temperature coefficient for the Cl atoms was found by trial.

After the last calculation of the structure factors, the disagreement index

$$R = \frac{\sum | |F_o| - |F_c| |}{\sum |F_o|}$$

amounted to 8.1%. In Table 1 the final values of F_c

Table 2. *Final atomic coordinates and temperature coefficients for ISbCl₈*

	Coordinates		
	x	y	z
I	0.754	0.848	0.1225
Sb	0.239	0.001	0.0000
Cl ₁	0.781	0.579	0.066
Cl ₂	0.570	0.688	0.186
Cl ₃	0.724	0.182	0.190
Cl ₄	0.942	0.110	0.040
Cl ₅	0.076	0.519	0.204
Cl ₆	0.263	0.756	0.065
Cl ₇	0.180	0.057	0.193
Cl ₈	0.400	0.214	0.058

Temperature coefficients

Sb, I:	$B_{xy} = 1.6$
	$B_z = 2.6$
Cl:	$B = 3.0$

are compared with F_o . The final coordinates and temperature coefficients are listed in Table 2 and in Fig. 1 the corresponding F_o synthesis is shown.

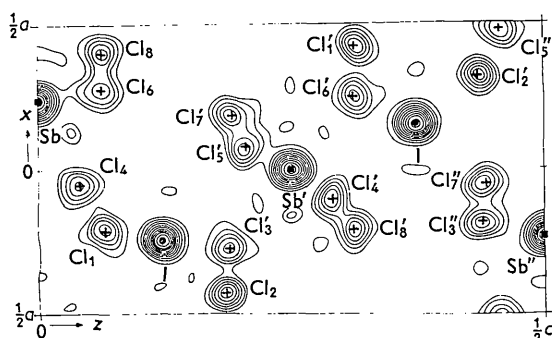


Fig. 1. ISbCl_6 ; Fourier synthesis of the [010] projection. Contourlines are drawn at 5, 10, 15 ... $\text{e.}\text{\AA}^{-2}$ in the maxima of the Cl atoms and at 5, 10, 20, 30 ... $\text{e.}\text{\AA}^{-2}$ in the maxima of the Sb and I atoms.

Also the structure factors F_{hko} were calculated from the final coordinates. The disagreement index, which amounted to 18% when the refinement of the [001] projection was stopped, decreased to 10.5%.

Accuracy

The standard deviations in the atomic coordinates were estimated from the $(F_o - F_c)$ values by the method of Cruickshank (1949). Because of the lack of a centre of symmetry in the [010] projection the values obtained from the structure factors F_{h0l} were doubled (Cruickshank, 1950). The following standard deviations in the atomic coordinates q , interatomic distances l and bond angles φ were found:

Sb and I	$\sigma(q) = 0.01 \text{ \AA}$
Cl	$\sigma(q) = 0.035$
Sb-Cl and I-Cl	$\sigma(l) = 0.04$
Cl-Cl	$\sigma(l) = 0.05$
$\angle \text{Cl-Sb-Cl}$ and $\angle \text{Cl-I-Cl}$	$\sigma(\varphi) = 1.4^\circ$

IAICl_6

IAICl_6 was prepared by heating equivalent amounts of ICl_3 and AlCl_3 in chloroform or carbontetrachloride as a solvent to about 100°C . in a sealed tube. After cooling, a crust of red IAICl_6 crystals had formed in the lower part of the tube. X-ray photographs were made of fragments of these crystals. Because of the very rapid decomposition of IAICl_6 in the open air these fragments were kept in thin-walled pyrex tubes. The photographs showed monoclinic symmetry.

Unit cell:

$$a = 6.92 \pm 0.03, \quad b = 11.02 \pm 0.05, \quad c = 6.11 \pm 0.03 \text{ \AA};$$

$$\beta = 99.1^\circ.$$

Reflections $0k0$ were absent for $k = 2n + 1$. The space group $P2_1$ was accepted because $P2_1/m$ was not in

agreement with the [100] Patterson synthesis. Density, calculated from the volume of the unit cell, assuming two IAICl_6 units per cell: 2.64 g.cm.^{-3} . Observed density $2.4 \pm 0.3 \text{ g.cm.}^{-3}$.

Intensities

Integrated and non-integrated Weissenberg photographs of the reflections $0kl$ were made from a needle-like crystal fragment for which the absorption of the employed $\text{Mo K}\alpha$ -radiation could be neglected. The same crystal was used to obtain the reflections $h0l$ on precession photographs.

Precession photographs were also made of the reflections hko . In this case a thin crystal slab was used which was irradiated transversely, so that the absorption was about equal for all reflections and could be neglected.

In this way the intensities of 75 reflections hko , 64 reflections $h0l$ and 89 reflections $0kl$ were obtained. The intensities from the precession photographs were corrected for Lorentz- and polarisation factors in the way described by Waser (1951).

Determination of the structure

The position of the I atom was found from Patterson syntheses of two of the main projections; approximate coordinates of the light atoms were obtained by the heavy-atom technique. This method was first applied to the centrosymmetric [010] projection, then to the non-centrosymmetric [001] projection in which the light-atom maxima have ghosts at centrosymmetric positions. It appeared that a structure consisting of tetrahedral AlCl_4^- ions and rectangular ICl_2^+ ions fitted the Fourier maps.

Refinement of the coordinates

At first the three main projections were refined separately by successive Fourier syntheses. The coordinates in the non-centrosymmetric projections were changed according to the double-shift rule. As however the separate refinement appeared to be difficult because of overlap of two or more atoms in each

Table 3. Final atomic coordinates and temperature coefficients for IAICl_6

	Coordinates		
	x	y	z
I	0.191	0.2500	0.007
Al	0.522	0.093	0.595
Cl ₁	0.993	0.211	0.266
Cl ₂	0.982	0.375	0.792
Cl ₃	0.808	0.045	0.694
Cl ₄	0.484	0.091	0.230
Cl ₅	0.672	0.467	0.309
Cl ₆	0.457	0.269	0.691

Temperature coefficients

I, Al:	$B = 3.0$
Cl:	$B = 4.0$

Table 4. *Experimental and calculated structure factors for AlCl₆*

<i>hkl</i>	$ F_o $	$ F_c $	α	<i>hkl</i>	$ F_o $	$ F_c $	α	<i>hkl</i>	$ F_o $	$ F_c $	α
100	12	12	0	480	16	13	301	055	10	12	1
200	18	19	0	580	23	25	22	056	10	12	26
300	70	69	180								
400	51	55	0	190	25	24	5	061	48	46	170
500	47	47	0	290	27	25	23	062	38	41	201
600	56	55	0	390	16	11	211	063	50	47	191
700	16	14	180	490	32	31	180	064	40	38	164
800	16	17	180					065	28	31	175
				0,10,0	24	32	216	066	12	14	191
110	72	78	0	1,10,0	22	20	140	067	17	14	185
210	51	47	320	2,10,0	39	41	345	068	10	9	174
310	26	23	161	3,10,0	23	22	1				
410	73	78	157					071	16	16	313
510	< 10	8	211	1,11,0	27	28	174	072	15	16	173
610	19	14	280	2,11,0	< 15	20	173	073	12	16	88
710	16	19	5	3,11,0	< 15	7	3	074	13	11	240
				4,11,0	19	18	329	075	8	9	211
020	78	80	161								
120	63	65	143	0,12,0	18	14	20	081	45	45	6
220	16	18	58	1,12,0	< 15	13	230	082	36	36	13
320	66	66	325	2,12,0	15	14	144	083	27	26	6
420	26	23	135	3,12,0	28	28	196	084	27	27	349
520	52	52	191					085	23	26	345
620	14	14	151	1,13,0	16	17	358	086	19	18	25
				2,13,0	16	15	21	087	< 8	9	1
130	100	111	178	0,14,0	16	17	173	088	11	7	343
230	53	50	214								
330	21	21	16	001	57	53	0	091	32	29	114
430	63	63	10	002	34	30	180	092	8	6	216
530	< 12	6	333	003	95	96	0	093	23	27	319
630	27	24	201	004	77	71	0	094	12	10	57
730	30	32	178	005	31	28	0				
				006	16	22	0				
040	81	87	16	007	23	22	0	0,10,1	33	31	174
140	43	44	300	008	14	8	0	0,10,2	25	28	160
240	74	77	172					0,10,3	31	30	183
340	67	71	231					0,10,4	22	17	182
440	16	16	131	011	< 3	10	225	0,10,5	9	8	193
540	47	42	351	012	52	55	66	0,10,6	18	18	184
640	14	16	2	013	24	22	255	0,10,7	11	10	175
740	< 15	14	222	014	21	26	291				
840	23	23	183	015	19	22	30	0,12,1	20	20	354
				016	11	14	64	0,12,2	28	28	359
								0,12,3	15	13	0
150	42	38	1	021	103	96	190	0,12,4	12	10	358
250	38	38	348	022	72	73	182	0,12,5	16	15	7
350	12	13	230	023	58	55	171				
450	46	46	174	024	51	53	178	0,14,1	16	12	170
550	< 14	12	301	025	31	33	176	0,14,2	14	12	177
650	16	16	349	026	27	25	206	0,14,3	14	16	209
				027	20	19	169	0,14,4	10	8	171
060	90	94	172	028	14	14	167				
160	57	56	80					0,16,0	7	4	47
260	12	10	46	031	75	70	265	0,16,1	11	12	359
360	67	70	10	032	16	15	97	0,16,2	11	12	350
460	25	25	151	033	36	40	123				
560	37	35	129	034	17	16	286	10 $\bar{6}$	27	19	0
660	23	22	167	035	10	12	194	10 $\bar{5}$	24	23	0
760	15	14	24	036	10	12	149	10 $\bar{4}$	30	35	0
								10 $\bar{3}$	14	13	0
170	66	68	172	041	60	60	351	10 $\bar{2}$	33	31	0
270	28	25	180	042	54	51	357	10 $\bar{1}$	66	65	0
370	23	22	18	043	81	86	1	101	54	55	0
470	37	40	355	044	40	44	354	102	< 12	10	0
570	14	15	28	045	11	7	65	103	< 14	5	180
670	23	17	177	046	32	31	358	104	25	26	0
770	23	21	163	047	21	24	358				
								20 $\bar{6}$	40	38	180
080	47	51	334	051	8	10	324	20 $\bar{5}$	< 16	7	180
180	18	18	30	052	30	32	315	204	< 16	9	0
280	23	25	228	053	18	17	101	20 $\bar{3}$	68	69	180
380	26	27	201	054	< 7	9	95	20 $\bar{2}$	106	112	180

Table 4 (cont.)

hkl	$ F_o $	$ F_c $	α	hkl	$ F_o $	$ F_c $	α	hkl	$ F_o $	$ F_c $	α
20 $\bar{1}$	23	21	180	304	< 14	5	180	502	25	24	0
201	100	99	180	305	30	26	180	503	30	28	0
202	68	72	180	306	16	19	180	504	34	37	0
203	42	43	180								
204	43	41	180	40 $\bar{1}$	25	22	180	60 $\bar{4}$	38	40	0
205	< 16	7	180	401	20	18	0	60 $\bar{3}$	26	19	0
206	26	24	180	402	28	31	180	60 $\bar{2}$	< 16	5	180
				403	< 14	4	0	60 $\bar{1}$	27	25	0
30 $\bar{7}$	20	24	180	404	26	23	0	601	< 16	4	0
30 $\bar{6}$	< 16	14	180	405	18	15	0	602	< 16	2	180
30 $\bar{5}$	38	32	180					603	25	21	0
304	50	50	180	50 $\bar{6}$	24	25	0				
30 $\bar{3}$	50	55	180	50 $\bar{5}$	22	21	0	703	10	14	180
30 $\bar{2}$	60	61	180	504	29	25	0				
30 $\bar{1}$	53	54	180	50 $\bar{3}$	40	36	0	80 $\bar{3}$	27	28	180
301	38	37	180	50 $\bar{2}$	29	30	0	80 $\bar{2}$	17	19	180
302	62	66	180	50 $\bar{1}$	50	56	0	80 $\bar{1}$	12	16	180
303	53	50	180	501	39	39	0	801	12	16	180

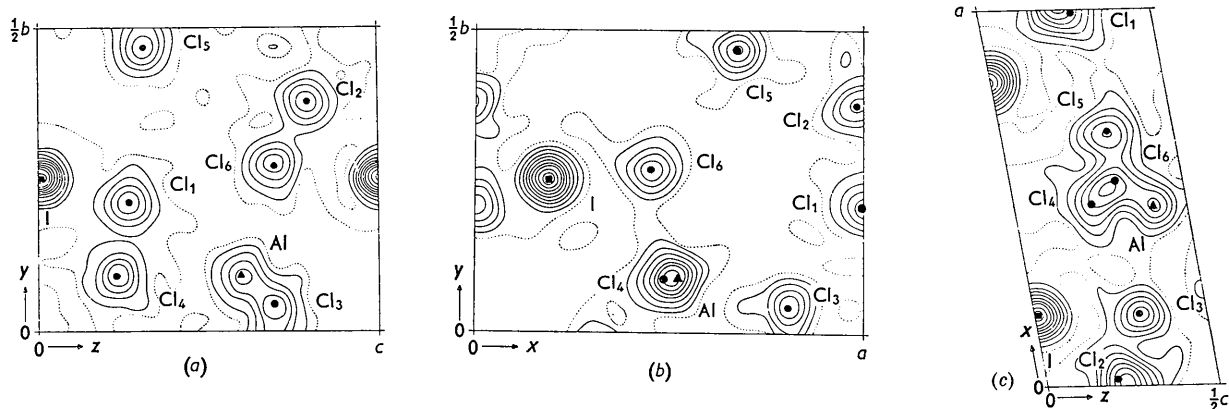


Fig. 2. IAlCl₆; Fourier syntheses of (a) [100], (b) [001] and (c) [010] projections. Contourlines are drawn at 5 (broken), 10, 15, 20 ... e.Å⁻² in the maxima of the Cl atoms and at 5 (broken), 10, 20, 30 ... e.Å⁻² in the maxima of the I atom.

projection, the final coordinates were determined by simultaneous refinement of the three projections. This means that one set of atomic coordinates was used for the calculation of the structure factors for all three projections, after which the corresponding shifts, following from the $(F_o - F_c)$ syntheses, were averaged.

After the second simultaneous structure factor calculation the shifts derived from the $(F_o - F_c)$ syntheses were contradictory in many cases and the refinement was not continued further. The disagreement indices for the three sets of structure factors were 6.2, 7.3 and 8.1% for the [001], [010] and [100] projection respectively. The temperature coefficients and the atomic coordinates which were used in the last structure-factor calculation are listed in Table 3, and in Fig. 2 the final Fourier syntheses of the three projections are given. Table 4 shows the observed and calculated structure factors.

Accuracy

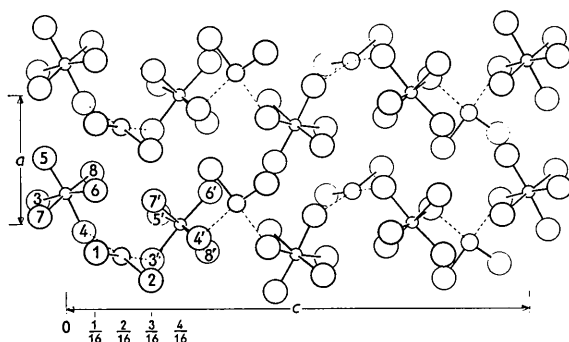
The standard deviations of the coordinates of the Cl and Al atoms calculated for the different projections yielded somewhat different values. Of these the

values obtained for the [100] projection were the highest. These were also considered to be the most reliable, since in this projection overlap of different atoms occurred only to a minor degree, whereas the number of reflections used for the Fourier syntheses of this projection was the largest. On the basis of these values the following standard deviations in the coordinates, interatomic distances and bond angles were finally assumed:

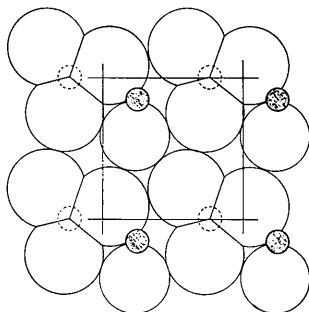
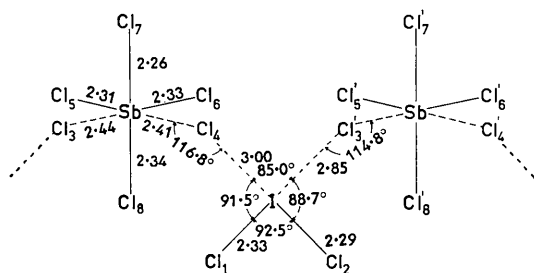
I	$\sigma(q) = 0.006 \text{ \AA}$
Cl	$\sigma(q) = 0.035$
Al	$\sigma(q) = 0.045$
I-Cl	$\sigma(l) = 0.04$
Al-Cl	$\sigma(l) = 0.06$
Cl-Cl	$\sigma(l) = 0.05$
\angle Cl-I-Cl	$\sigma(\varphi) = 1.4^\circ$
\angle Cl-Al-Cl	$\sigma(\varphi) = 2.4^\circ$

Discussion of the structures

The structure of ISbCl₈ is shown in Fig. 3. It can be considered as consisting of layers of Cl atoms between

Fig. 3. Structure of ISbCl_3 as viewed along $[010]$.

which the Sb and I atoms are located. Perpendicular to the tetragonal screw axes there are two crystallographically different sets of Cl layers: those at $z = \frac{1}{16}c$, $\frac{5}{16}c$, etc. and those at $z = \frac{3}{16}c$, $\frac{7}{16}c$ etc. Layers of the same set are identical because of the tetragonal screw axes. Though there are no symmetry relations between the two sets of layers they are still almost identical. The mean difference of the positions of the Cl atoms with respect to each other in the two kinds of layers is only 0.16 \AA . The arrangement of the Cl atoms in the layers is shown in Fig. 4.

Fig. 4. Packing of Cl atoms in a layer perpendicular to $[010]$ in ISbCl_3 . The I atoms just above and the Sb atoms just below the layer are indicated by small full and broken circles respectively.Fig. 5. Main bond lengths and bond angles in ISbCl_3 .

Bond angles					
$\text{Cl}_3\text{-Sb-Cl}_4$	81.6°	$\text{Cl}_4\text{-Sb-Cl}_6$	91.3°	$\text{Cl}_5\text{-Sb-Cl}_7$	93.1°
$\text{Cl}_3\text{-Sb-Cl}_5$	91.0	$\text{Cl}_4\text{-Sb-Cl}_7$	86.5	$\text{Cl}_5\text{-Sb-Cl}_8$	91.6
$\text{Cl}_3\text{-Sb-Cl}_7$	88.9	$\text{Cl}_4\text{-Sb-Cl}_8$	88.3	$\text{Cl}_5\text{-Sb-Cl}_7$	92.4
$\text{Cl}_3\text{-Sb-Cl}_8$	86.5	$\text{Cl}_5\text{-Sb-Cl}_6$	95.2	$\text{Cl}_6\text{-Sb-Cl}_8$	91.5

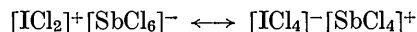
At first sight the structure of ISbCl_3 can be considered as an ionic structure consisting of ICl_2^+ ions which are almost rectangular, and SbCl_6^- ions with a distorted octahedral configuration. The rectangular shape of the ICl_2^+ ions is to be expected from the electronic configuration of the I^+ ions: the two unpaired $5p$ electrons of this ion may be used for the bonds with the Cl atoms.

The main interatomic distances and bond angles are indicated in Fig. 5. From an examination of these distances it follows that there is a special interaction between the ICl_2^+ and the SbCl_6^- ions. The distances I-Cl_3 and I-Cl_4 are larger than the I-Cl distances in the ICl_2^+ ions, but appreciably shorter than the sum of the van der Waals radii (3.9 \AA). Apparently weak bonds are present between the ICl_2^+ and SbCl_6^- ions, by which these ions are linked to chains parallel to the z -axis of the crystal. In Fig. 5 these bonds are indicated by broken lines.

It further follows from Fig. 5 that the lengths of the bonds Sb-Cl_3 and Sb-Cl_4 are larger than those of the other bonds in the SbCl_6^- ion. From a χ^2 -test (Cruickshank & Robertson, 1953) it was concluded that these differences are significant.

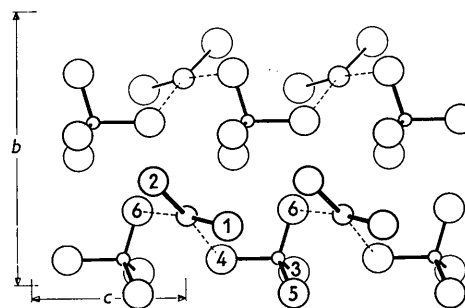
Finally it is noticeable that the Cl-I-Cl angles in the group of atoms $\text{I, Cl}_1, \text{Cl}_2, \text{Cl}_3$ and Cl_4 are all about 90° and that this group is almost planar. Using the method of the least squares (with different weights for the I and Cl atoms) the deviations from coplanarity for the atoms of the group were found to be $0.02, -0.18, 0.01, 0.02$ and -0.13 \AA respectively. Hence, apart from the difference in the I-Cl distances, the configuration of this group is very similar to that of the ICl_4^- ion, in which the Cl atoms are located at the corners of a square around the I atom (Mooney, 1938).

These observations indicate that the structure of ISbCl_3 is intermediate between the structures $[\text{ICl}_2]^+[\text{SbCl}_6]^-$ and $[\text{ICl}_4]^-[\text{SbCl}_4]^+$. In the terminology of the valence-bond method the structure may be represented as a mesomerism according to the scheme



in which the first predominates.

The structure of IAICl_6 , which is shown in Fig. 6, is similar to the structure of ISbCl_3 in many respects.

Fig. 6. Structure of IAI_6 as viewed along $[100]$.

In this compound there are Cl layers parallel to (001). Because of the diad screw axis the layers are however all identical in this case.

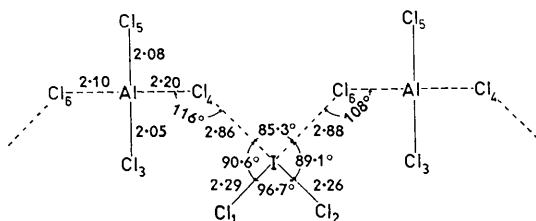


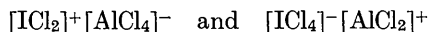
Fig. 7. Main bond lengths and bond angles in IAICl₆.

Bond angles	
Cl ₄ -Al-Cl ₆	106.8°
Cl ₄ -Al-Cl ₃	104.5
Cl ₄ -Al-Cl ₅	107.4
Cl ₆ -Al-Cl ₃	113.4°
Cl ₅ -Al-Cl ₃	111.3
Cl ₃ -Al-Cl ₅	112.5

As can be seen from Fig. 7, in which the main interatomic distances and bond angles are given, the structure [ICl₂]⁺[AlCl₄]⁻ prevails in IAICl₆. The ICl₂⁺ ions have the same configuration as in ISbCl₃, whereas the AlCl₄⁻ ions have an approximately tetrahedral configuration.

The distances I-Cl₄ and I-Cl₆ are about the same as the corresponding distances in ISbCl₃. Apparently the ICl₂⁺ and AlCl₄⁻ ions are linked by weak bonds to chains parallel to [001]. Again the shape of the group I, Cl₁, Cl₂, Cl₄, Cl₆ is similar to that of an ICl₄⁻ ion. The deviations of the atoms from the nearest plane are 0.004, -0.09, -0.03, -0.03 and 0.07 Å respectively.

Therefore the structure of IAICl₆ may be represented by a resonance between the structures

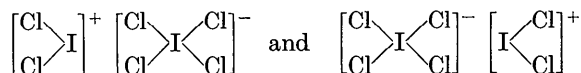


in which the first predominates.

The extension of the bonds Al-Cl₄ and Al-Cl₆ which is to be expected from this resonance, is difficult to observe in this case because of the high standard deviation which had to be assigned to the Al-Cl

distances. Actually these bonds are found to be somewhat longer than the other two Al-Cl bonds in the AlCl₄⁻ ion, but the differences are not significant.

A similar mesomerism as assumed in ISbCl₃ and IAICl₆ was used by Boswijk & Wiebenga (1954) to describe the structure of iodine trichloride. The structure of the flat I₂Cl₆ molecules of which this compound consists was represented by a mesomerism between the structures:



In contradistinction to the case of ISbCl₃ and IAICl₆ the two structures will here contribute to the same extent, which explains that the distance between the I atoms and the central Cl atoms in I₂Cl₆ (2.70 Å) is smaller than the corresponding distances I-Cl₃, I-Cl₄ in ISbCl₃ and I-Cl₄, I-Cl₆ in IAICl₆ (mean value 2.9 Å).

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References

- BOSWIJK, K. H. & WIEBENGA, E. H. (1954). *Acta Cryst.* **7**, 417.
 CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
 CRUICKSHANK, D. W. J. (1950). *Acta Cryst.* **3**, 72.
 CRUICKSHANK, D. W. J. & ROBERTSON, A. P. (1953). *Acta Cryst.* **6**, 698.
 MOONEY, R. C. L. (1938). *Z. Kristallogr.* **98**, 377.
 VONK, C. G. (1959). *Rec. Trav. Chim. Pays-Bas*. To be published.
 WASER, J. (1951). *Rev. Sci. Instrum.* **22**, 567.
 WOOLF, A. A. & EMELÉUS, H. J. (1949). *J. Chem. Soc.* p. 1865.