335. *The Crystal Structure of Gallium Trichloride*

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Gallium trichloride forms triclinic crystals with 2 Ga and 6 Cl in each unit cell of dimensions $a = 6{\cdot}94$, $b = 6{\cdot}84$, $c = 6{\cdot}82$, all $\pm 0{\cdot}02$ Å, $\alpha = 119{\cdot}5^\circ$, $\beta = 90{\cdot}8^\circ$, $\gamma = 118{\cdot}6^\circ$, all $\pm 0{\cdot}5^\circ$, and space group $P\bar{1}$. Dimer molecules, Ga_2Cl_6, are so arranged as to cause the chlorine atoms to form approximately close-packed sheets with one quarter of the sites unoccupied and with gallium atoms in half of the intervening tetrahedral sites. Movement of Ga^{3+} and Cl^- ions among the vacant sites might explain the enhanced electrical conductivity of the solid compared with that of the liquid.

Gallium occupies a position in the Periodic Table between those elements which form typically ionic compounds and those which form typically covalent compounds. The properties of the trichloride illustrate this intermediate position. It melts at 78° to give a slightly conducting liquid, suggesting largely covalent character, but the conductivity of the solid at the melting point is higher than that of the liquid.[1] This unusual property is also found in aluminium trichloride and phosphorus pentachloride, both of which are ionic in the solid state but mainly covalent in the liquid state. Unlike these two compounds, however, gallium trichloride does not exhibit a large decrease in density on melting. This indicates that there is a much smaller change in structure on melting than in the cases of aluminium trichloride and phosphorus pentachloride. The crystal structure of gallium trichloride has therefore been determined as a contribution to the understanding of its properties.

Other structural techniques have provided evidence for dimer molecules, Ga_2Cl_6, in each of the three phases. Electron diffraction of the vapour[2] showed Ga_2Cl_6 molecules

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[1] N. N. Greenwood and I. J. Worrall, *J. Inorg. Nuclear Chem.*, 1957, **3**, 357.

[2] P. A. Akishin, V. A. Naumov, and V. M. Tatevskii, *Kristallografiya*, 1959, **4**, 194.

in the form of two tetrahedra sharing one edge with dimensions Ga–Cl_p (p = peripheral) 2·09 Å, Ga–Cl_b (b = bridging) 2·29 Å, $\angle Cl_p$–Ga–Cl_p 112 ± 3°, $\angle Cl_b$–Ga–Cl_b 89 ± 3°. Raman spectra of the solid and liquid have been interpreted in terms of molecular dimers,[3] and lines attributable to Ga_2Cl_6 molecules have been seen in the Raman spectrum of gallium trichloride dissolved in phosphorus trichloride.[4] Nuclear quadrupole resonance measurements on solid gallium trichloride [5] have been interpreted in terms of dimer molecules with the Ga–Cl_b bonds weaker than the Ga–Cl_p bonds which are estimated to have about 50% ionic character.

EXPERIMENTAL

Gallium trichloride was prepared by heating metallic gallium in a stream of chlorine, and purified by sublimation twice in an atmosphere of chlorine and twice *in vacuo*. For *X*-ray photography the colourless crystalline material was sublimed *in vacuo* into thin-walled Pyrex capillary tubes which were then sealed off and mounted on a Weissenberg goniometer. Difficulty was experienced in orientating the crystals so as to rotate about a crystallographic axis because (a) only a limited range of orientations could be explored satisfactorily for a given crystal in a capillary, (b) the crystals were easily lost by re-sublimation, (c) the crystal face development was complex, so that crystal directions could not be recognized visually, (d) twinning caused extra symmetry in the diffraction pattern, and (e) all three cell lengths were very similar. Eventually, satisfactory Weissenberg photographs for intensity estimation were obtained only for the zero and first layers for rotation of the crystal about the *a*-axis. Poorer quality photographs about various other axes were used for confirmation of the crystal symmetry and for the determination of cell dimensions. Intensities of the $0kl$ and $1kl$ intensities were estimated visually and converted into structure amplitude (F_0) values in the usual way. No correction was made for *X*-ray absorption in the specimen in view of the irregular crystal shape ($\mu t_{\text{max.}} \sim 10$).

STRUCTURE DETERMINATION

The crystal data are as follows: Ga_2Cl_6, $M = 352·2$, m. p. 78°. Triclinic, space group $P\bar{1}$, $a = 6·94$, $b = 6·84$, $c = 6·82$, all $\pm 0·02$ Å, $\alpha = 119·5°$, $\beta = 90·8°$, $\gamma = 118·6°$, all $\pm 0·5°$; $a^* = 0·1738$, $b^* = 0·2024$, $c^* = 0·1783$, all $\pm 0·0005$ Å^{-1}, $\alpha^* = 55·3°$, $\beta^* = 70·9°$, $\gamma^* = 56·0°$, all $\pm 0·5°$; $U = 234$ Å^3, $D_m = 2·47$, $Z = 1$, $D_c = 2·50$, $F(000) = 164$, $\mu = 226$ cm.$^{-1}$, (CuK_α, $\lambda = 1·542$ Å).

In the initial stages of the analyses difficulty was experienced in determining the crystal system. Photographs with *a* as the rotation axis gave the appearance of monoclinic symmetry, but slight splitting of the spots on the higher layers into pairs with different intensities revealed that the apparent monoclinic symmetry was due to twinning. There were no systematic absences amongst the *X*-ray reflections, and since there was no indication of symmetry in the diffraction pattern of each member of the twin the crystal was assigned to the triclinic system. A search for an untwinned crystal for intensity measurement was unsuccessful. The intensities of the *a*-axis zero-layer reflections are unaffected by the twinning because the $0kl$ level of the reciprocal lattice is common to both twins. The corresponding first layer Weissenberg photograph, however, contains both $1kl$ and $\bar{1}kl$ reflections occurring in pairs either in close proximity or overlapping. Separate intensities were estimated where this was possible, otherwise a combined intensity was measured.

Because the crystals were hydrolysed rapidly by atmospheric moisture they could not be handled in the atmosphere and it was not possible to carry out physical tests for the presence or absence of a centre of symmetry. Both the $N(z)$ and the $\langle z^2 \rangle$ and $\langle z^3 \rangle$ statistical tests [6,7] on the measured $0kl$ intensities were inconclusive. Since there are only two of the heavier Ga atoms in each unit cell there must be at least a pseudo-centre of symmetry between these, so the space group was assumed to be $P\bar{1}$. In the subsequent structure analysis no evidence for a

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[3] H. Gerding, H. G. Haring, and P. A. Renes, *Rec. Trav. chim.*, 1953, **72**, 78.

[4] N. N. Greenwood, P. G. Perkins, and K. Wade, *J.*, 1957, 4345.

[5] H. G. Dehmelt, *Phys. Rev.*, 1953, **92**, 1240; P. A. Casabella, P. J. Bray, and R. G. Barnes, *J. Chem. Phys.*, 1959, **30**, 1393.

[6] E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Cryst.*, 1950, **3**, 210.

[7] F. Foster and A. Hargreaves, *Acta Cryst.*, 1963, **16**, 1133.

non-centrosymmetric arrangement of the chlorine atoms appears so the assumption of $P\bar{1}$ was justified.

The *a*-axis projection of the structure was solved in terms of a Ga_2Cl_6 molecule by comparing information obtained from the $0kl$ Patterson projection with the $0kl$ weighted reciprocal lattice. The atomic *y*- and *z*-co-ordinates were then partly refined by Fourier methods. The *x*-co-ordinates were obtained from generalised C_1 and S_1 Patterson and Fourier syntheses. The difficulty of having only a combined intensity for 18 of the 63 pairs of $1kl$ and $\bar{1}kl$ reflections did not affect the C_1 generalised Patterson projection because the sums $F_{1kl}^2 + F_{\bar{1}kl}^2$ are required for the calculation. For the S_1 Patterson synthesis, where the corresponding differences are required, the differences for the unresolved pairs of reflections were taken as zero. The appropriate *x*-co-ordinates obtained from the resulting C_1 and S_1 Patterson maps were found to be consistent with a molecular model of expected dimensions orientated in one of the two ways indicated by the $0kl$ electron-density map. For the Fourier C_1 and S_1 generalised projections the unresolved $1kl$ and $\bar{1}kl$ reflections were given F_o values by dividing the total F_o^2 in the same ratio as the values of F_c^2.

Final refinement of the *x*-, *y*-, and *z*-co-ordinates and isotropic temperature factors was carried out by the least-squares method using Rollett's S.F.L.S. programme[8] for the MERCURY computer. In the later stages of this refinement the F_o values for all the 65 $0kl$ reflections and for 59 of the $1kl$ and $\bar{1}kl$ reflections were given individual weights on the basis of the size of F_o and the degree of resolution of the pairs of spots on the higher-layer photographs. Unresolved and poorly resolved reflections were omitted. Convergence was reached with a disagreement index, *R*, for the 124 reflections of 0·13.

RESULTS AND DISCUSSION

The final atomic positions from the least-squares analysis and their standard deviations calculated from the normal-equations matrix are shown in Table 1, together with the final isotropic temperature factors. A Fourier $0kl$ projection calculated from the signs obtained in the final structure factor calculation is shown in Fig. 1 together with the molecule indicated in the position obtained by the least-squares analysis. A comparison of final F_o and F_c values is shown in Table 2.

TABLE 1

Final atomic co-ordinates as fractions of the unit-cell lengths, their standard deviations (in Å), and isotropic temperature factors (in Å²)

Atom	x/a	σx	y/b	σy	z/c	σz	B
Ga	0·218	0·03	0·071	0·01	0·159	0·01	1·6
Cl(1)	−0·032	0·07	0·233	0·02	0·234	0·02	3·1
Cl(2)	0·554	0·07	0·360	0·02	0·190	0·02	3·1
Cl(3)	0·184	0·07	−0·129	0·02	0·315	0·02	3·1

The *X*-ray data used in this structure analysis were neither sufficiently complete nor sufficiently accurate to provide reliable molecular dimensions, but Fig. 2 shows the approximate dimensions obtained by taking a weighted average of chemically similar bonds (weighted in inverse proportion to their standard deviations). The two Ga, Cl(2), Cl(3) planes of the molecule are coplanar and at right angles to the Ga, Cl(1), Ga', Cl(1') plane, within experimental error. The errors shown are based on the weighted deviations from the mean of the values averaged but they are of the same order of size as the errors indicated by the standard deviations in the atomic positions. The averaged dimensions are in fair agreement with the electron-diffraction dimensions quoted above for the gaseous molecule.

The basically covalent nature of gallium trichloride in the solid state has been established by the recognition of separate molecules in the crystal lattice. This is in agreement with the low melting point and the lack of any large change in density on melting. The question

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[8] R. Pepinsky, J. M. Robertson, and J. C. Speakman, "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," Pergamon, Oxford, 1961, p. 107.

TABLE 2

Comparison of observed and final calculated structure factors
(The values in parentheses were omitted from the least-squares refinement)

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
001	31	33	$03\bar{1}$	33	29	$06\bar{5}$	14	−14	123	(25)	(26)	$15\bar{2}$	(7)	(9)	$\bar{1}3\bar{4}$	(13)	(−18)
002	84	−75	$03\bar{2}$	60	47	$06\bar{6}$	11	−9	124	(16)	(21)	$15\bar{4}$	16	15	$\bar{1}3\bar{3}$	31	−24
003	45	−43	$03\bar{3}$	14	−11	$07\bar{3}$	21	25	$12\bar{1}$	24	20	$15\bar{5}$	12	12	$\bar{1}3\bar{7}$	(24)	(21)
004	10	−10	$03\bar{4}$	48	−44	$07\bar{4}$	6	11	$12\bar{2}$	80	71	$15\bar{6}$	16	−17	$\bar{1}40$	(47)	(44)
005	16	11	$03\bar{5}$	20	−19	$07\bar{5}$	14	−17	$12\bar{3}$	49	41	$15\bar{7}$	18	−19	$\bar{1}41$	(16)	(8)
006	12	20	$03\bar{7}$	15	16	$07\bar{6}$	11	−15	$12\bar{4}$	37	−40	$16\bar{4}$	21	20	$\bar{1}42$	(20)	(−16)
010	54	55	$03\bar{8}$	17	15	$07\bar{7}$	5	−2	$12\bar{5}$	37	−40	$16\bar{5}$	15	15	$\bar{1}43$	(22)	(−23)
011	35	−31	040	17	−15	100	22	25	$12\bar{7}$	(7)	(7)	$\bar{1}10$	33	30	$\bar{1}4\bar{1}$	36	36
012	65	−55	041	19	−20	101	45	−56	130	(33)	(−38)	$\bar{1}11$	73	77	$\bar{1}4\bar{2}$	(33)	(−35)
014	13	10	042	16	−12	102	37	−35	132	(7)	(6)	$\bar{1}12$	10	19	$\bar{1}4\bar{3}$	47	−45
$01\bar{1}$	54	65	$04\bar{1}$	30	23	103	(1)	(1)	133	(11)	(11)	$\bar{1}13$	(21)	(23)	$\bar{1}4\bar{6}$	(3)	(3)
$01\bar{2}$	30	31	$04\bar{2}$	49	39	104	(14)	(12)	$13\bar{1}$	54	−43	$\bar{1}14$	(28)	(−24)	$\bar{1}4\bar{7}$	(16)	(14)
$01\bar{3}$	30	−32	$04\bar{3}$	12	10	105	(20)	(19)	$13\bar{2}$	(43)	(38)	$\bar{1}15$	(20)	(−20)	$\bar{1}51$	(22)	(−23)
$01\bar{4}$	53	−58	$04\bar{4}$	11	−9	$10\bar{1}$	37	49	$13\bar{3}$	93	69	$\bar{1}1\bar{1}$	25	−32	$\bar{1}52$	(18)	(−19)
$01\bar{6}$	26	27	$04\bar{5}$	27	−28	$10\bar{3}$	8	14	$13\bar{4}$	(10)	(5)	$\bar{1}1\bar{2}$	33	−40	$\bar{1}5\bar{1}$	47	48
$01\bar{7}$	8	13	$04\bar{6}$	31	−29	$10\bar{5}$	26	−33	$13\bar{5}$	31	−31	$\bar{1}1\bar{3}$	39	−44	$\bar{1}5\bar{3}$	31	−28
020	6	3	$04\bar{7}$	8	10	$10\bar{6}$	(14)	(−15)	$13\bar{6}$	(23)	(−26)	$\bar{1}1\bar{5}$	41	43	$\bar{1}5\bar{4}$	27	−30
021	15	12	$04\bar{8}$	26	27	$10\bar{7}$	(8)	(13)	$13\bar{7}$	(11)	(−9)	$\bar{1}1\bar{6}$	(17)	(18)	$\bar{1}5\bar{5}$	20	−15
022	19	−19	050	9	−11	110	38	38	140	(26)	(−12)	$\bar{1}1\bar{7}$	(7)	(−12)	$\bar{1}5\bar{6}$	16	15
023	20	−20	051	16	−17	111	64	−56	141	(3)	(3)	$\bar{1}21$	30	36	$\bar{1}5\bar{7}$	(16)	(23)
024	10	−2	$05\bar{1}$	18	16	112	40	−45	142	(1)	(−1)	$\bar{1}24$	(21)	(−18)	$\bar{1}6\bar{1}$	(10)	(13)
$02\bar{2}$	55	50	$05\bar{2}$	14	12	113	(33)	(12)	$14\bar{1}$	20	−21	$\bar{1}2\bar{1}$	31	29	$\bar{1}6\bar{2}$	(15)	(18)
$02\bar{4}$	53	−51	$05\bar{4}$	16	12	114	(22)	(18)	$14\bar{3}$	22	20	$\bar{1}2\bar{2}$	(19)	(12)	$\bar{1}6\bar{4}$	23	−21
$02\bar{5}$	15	−14	$05\bar{6}$	28	−27	$11\bar{1}$	52	55	$14\bar{4}$	25	21	$\bar{1}2\bar{3}$	55	−64	$\bar{1}6\bar{5}$	26	−30
$02\bar{6}$	18	14	$05\bar{8}$	14	12	$11\bar{5}$	19	−18	$14\bar{5}$	16	9	$\bar{1}2\bar{4}$	35	−37	$\bar{1}6\bar{7}$	14	16
$02\bar{7}$	11	10	060	12	−13	$11\bar{6}$	(4)	(−4)	$14\bar{6}$	20	−22	$\bar{1}2\bar{5}$	29	26	$\bar{1}7\bar{4}$	10	−12
030	10	5	$06\bar{1}$	11	10	120	40	−29	$14\bar{7}$	(25)	(−24)	$\bar{1}2\bar{6}$	(30)	(31)	$\bar{1}7\bar{5}$	15	−19
032	30	−28	$06\bar{2}$	16	16	121	55	−53	150	(17)	(−19)	$\bar{1}31$	32	29			
033	24	−22	$06\bar{3}$	11	10	122	22	−19	$15\bar{1}$	(5)	(−7)	$\bar{1}33$	(27)	(−28)			

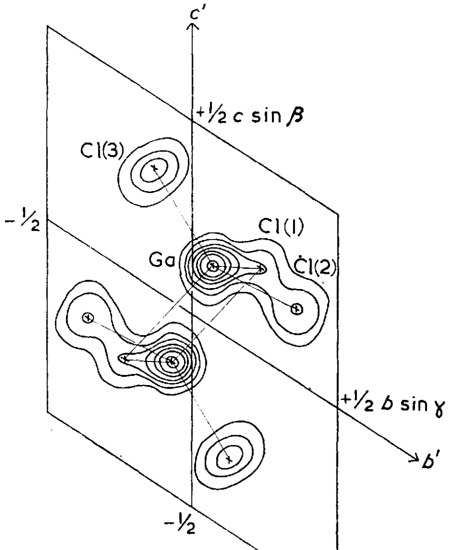

FIG. 1. Final 0*kl* Fourier electron-density projection (contours at 5, 15, 25, . . . eÅ^{-2}; crosses indicate final least-squares atomic positions)

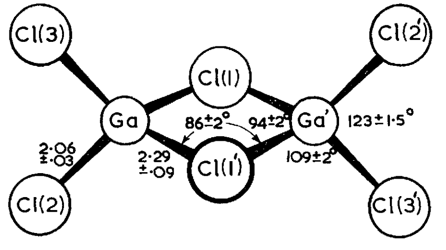

FIG. 2. Average dimensions for a Ga_2Cl_6 molecule of *mmm* symmetry

therefore arises as to whether the crystal structure offers any explanation for the observed electrical conductivity of the solid.

When the structural arrangement is examined from the point of view of the packing of chlorine atoms, it is found that it can be described in terms of distorted hexagonal close-packing. (The average intra- and inter-molecular Cl · · · Cl distances are 3·59 and 3·61 Å, respectively.) Approximately close-packed layers of chlorine atoms are arranged parallel to (001) and at $z = \pm\frac{1}{4}$. However, in each layer one quarter of the close-packed positions is unoccupied, so that each of the two peripheral chlorine atoms makes eight instead of twelve contacts with adjacent chlorine atoms. This suggests that the possession of a partial negative charge by these atoms is the probable reason for not forming a complete close-packed structure, especially since only four of the eight contacts are with other peripheral chlorine atoms. The vacant sites in adjacent layers are so arranged as to give channels running through the structure parallel to [011]. Fig. 3 shows the positions of the chlorine atoms in two centrosymmetrically related adjacent layers. The distortion from regular close-packed positions can be seen, and also the beginning of the formation of the channel. The gallium atoms occur in tetrahedral sites between these two layers, in the tetrahedra whose edges are all shown in Fig. 3. If the close-packed layers had been complete, one eighth of the tetrahedral sites would have been occupied corresponding to a MX_4 structure. The vacant sites restore the stoicheiometry to the required MX_3, and, in fact, half of the tetrahedral sites which still exist in the structure are occupied by gallium atoms. These facts show that there is room in the structure for interstitial atoms or ions of gallium and chlorine, each occupying a site where it would have similar co-ordination to that of atoms already present.

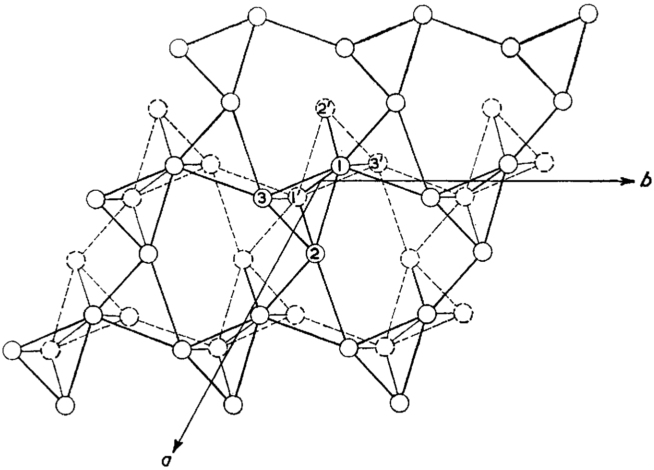

FIG. 3. Two adjacent layers of chlorine atoms projected on to the (001) plane

A possible explanation of the conductivity of the solid is that the structure may contain interstitial ions or may develop them under the influence of an applied electric field (cf. the 50% ionic character in the peripheral Ga–Cl bonds suggested by the nuclear quadrupole resonance results) and that these might be able to move to adjacent similar sites and so continue through the whole structure. Movement of ions along the channel caused by the vacant sites in the approximately close-packed chlorine atom layers would take place more readily than the transfer of gallium atoms between occupied and unoccupied tetrahedral sites through triangular groups of approximately close-packed chlorine atoms. If this explanation of the conductivity is correct, it might be possible to show experimentally that it takes place preferentially along the [011] crystal direction.

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