Crystal Structures of the Supramolecular Aggregates of the Methyl and Chloro Substituted Gallanes Me_xGaCl_{3-x}

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Dedicated to Professor Ingo-Peter Lorenz on the occasion of his 60th birthday

The crystal structures of the complete series of compounds of the general formula Me_xGaCl_{3-x} have been determined. New polymorphs of $GaCl_3$ and $MeGaCl_2$ were found. All chloro compounds Me_xGaCl_{3-x} ($x = 0, 1, 2$) are dimers with Ga_2Cl_2 four-membered rings. $(GaCl_3)_2$ and $(MeGaCl_2)_2$ are aggregated into layers with the same aggregation motif (each molecule connected to four neighbouring molecules), $(Me_2GaCl)_2$ is associated in a ladder-like structure (each molecule connected to two neighbouring molecules), $GaMe_3$ forms weakly $Ga\cdots C$ bound pseudo-tetramers aggregated into layers by further $Ga\cdots C$ contacts (each molecule has two shorter $Ga\cdots C'$ and $C\cdots Ga'$ and two weaker $Ga\cdots C'$ and $C\cdots Ga'$ contacts).

Key words: Gallium, Crystal Structure, Supramolecular Chemistry, Aggregation

Introduction

Aggregation of group 13 compounds through self-assembly is a common phenomenon. Most frequently halogen atoms are involved in the aggregation, in particular the softer donors (Cl, Br, I) [1]. Complexation through Lewis acid-base interactions are the primary step in the self-assembly of organo group 13 halides, usually forming four-membered M_2X_2 rings, which are even observed in the gas phase, *e.g.* in Al_2Cl_6 [2]. Significantly weaker interactions between these primary adducts lead to an increase in the coordination numbers of the metal centres, usually to five, but higher coordination numbers are known [1]. Typical motifs of aggregation are depicted in Scheme 1: simple dimers (A), ladder structures of polymerised dimers (B), ladder structures resulting from a chain formed by stronger acid base interactions plus weaker secondary interactions (C), true ladder structures with $M\cdots X$ interactions of the same length (D), chains with two pairs of intermolecular interactions of similar strength (E) and more complicated networks with six-coordinate metal atoms (F).

For an elucidation of the principles behind the different types of aggregation a detailed knowledge of the simplest representatives of a series of closely related
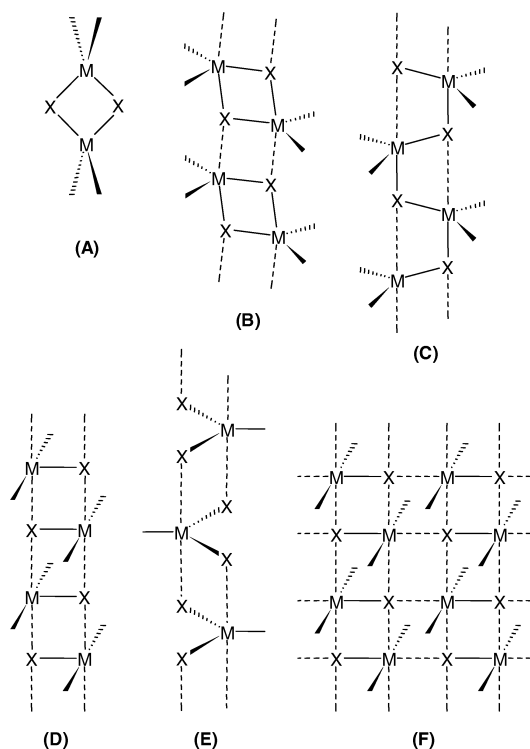
Scheme 1.

	Lengths				Angles		
	XRD	XRD[old]	GED		XRD	XRD[old]	GED
Ga-Cl1	2.290(1)	2.29(2)	2.298(6)	Cl2-Ga-Cl3	122.2(1)	123(1.5)	124.5(1)
Ga-Cl2	2.091(2)			Ga1'-Cl2-Ga	90.1(1)	86(2)	90(1)
Ga-Cl3	2.112(1)	2.06(3)	2.093(5)	Cl1-Ga-Cl2	111.1(1)		
Ga···Cl3"	3.721(1)			Cl1-Ga-Cl3	108.9(1)	109(2)	
				Cl1-Ga-Cl1'	89.9(1)		
				Cl2-Ga-Cl4	111.1(1)		

Table 1. Selected bond lengths [Å] and angles [°] of gallium trichloride in comparison with the results of the earlier crystal structure determination [5] and the gas phase structure of $GaCl_3$ [6].

compounds is required. Molecular simplicity in this context means studying compounds with the smallest possible organic groups attached to the metal centres in order to reduce unpredictable effects of steric repulsion between bulky substituents and involvement of further van der Waals attractive forces between these groups or conformational effects of larger alkyl groups. In our current investigations of compounds with group 13 elements in geminal position to donor centres [3], we frequently use Me_xGaCl_{3-x} compounds as starting materials and therefore were in a position to determine the crystal structures of the whole series, which we report in this paper. The crystal structures of trimethyl- and triethylgallium were already reported by us in a preliminary communication together with the unique cryo-triboluminescent behaviour of triethylgallium [4].

Results and Discussion

Crystal structure of gallium trichloride

The structure of gallium trichloride in the solid state was already reported in 1965, but the authors already admitted that the structure determination was of low quality and only suitable for an elucidation of the constitution [5]. In this early structural study $GaCl_3$ was found to crystallize in the space group $P\bar{1}$, but the determination was based on diffraction data of a twinned crystal. The single crystals of $GaCl_3$ in our hands stemmed from a commercial sample sealed in a glass ampoule under vacuum from which they grew upon sublimation over several years. They belong to the monoclinic space group $C2/m$. The new cell dimensions [a, b, c, β: 11.9152(5), 6.8128(4), 7.0258(3) Å, 125.749(3)°] do not suggest a structural relationship to the earlier ones [$a, b, c, \alpha, \beta, \gamma$: 6.94(2), 6.84(2), 6.82(2) Å, 119.5(5), 90.8(5), 118.6(5)°]. In the phase now investigated $GaCl_3$ forms dimeric molecules Ga_2Cl_6, which are close to overall D_{2h} symmetry (Fig. 1). Two chlorine bridges link the two gallium centres and this parallels the situation in gaseous $GaCl_3$ where these dimers are also present, at least up to a temperature of 322 K at which already
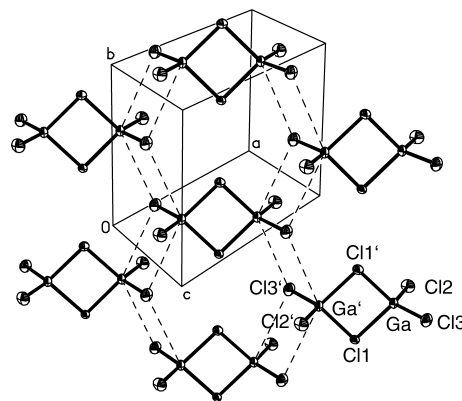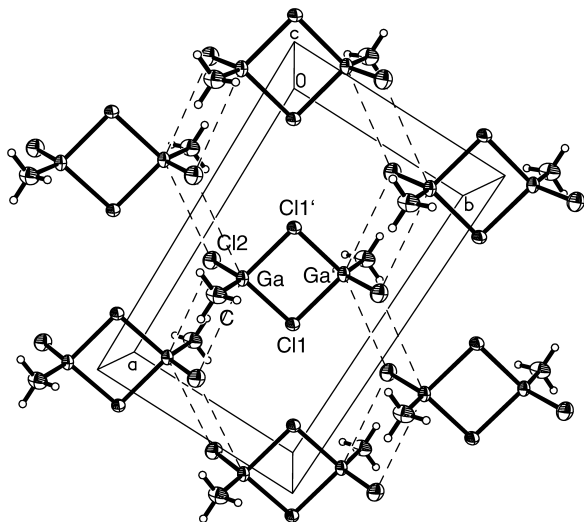

Fig. 1. Crystal structure and cell of $(GaCl_3)_2$. The dashed lines represent the shortest intermolecular Ga···Cl contacts.

21 mol% of the vapour consist of monomeric $GaCl_3$ [6]. At higher temperatures a complex mixture of gas phase species has been observed experimentally [7]. Note, however, that solid $AlCl_3$ forms a typical ionic lattice with layers of chloride anions and octahedrally coordinated Al cations in the interstices [8], but in the gas phase at temperatures not far above the sublimation point $AlCl_3$ is also present as dimeric Al_2Cl_6 [2].

For comparison the new solid state geometrical data of $GaCl_3$ are listed in Table 1 in comparison to the literature data from 1965 and to the gas phase parameters refined for a D_{2h} symmetrical structure [6]. The structures in the solid and the gas phase are reasonably similar *i. e.* there are only slight distortions of the Ga_2Cl_6 units in the solid state. These distortions are the result of weak Ga···Cl interactions (3.721 Å), which lead to the formation of a layer structure (Fig. 1) with (4+2)-coordinate Ga atoms. The primary coordination geometry of gallium is that of a strongly distorted tetrahedron, with a large angle of 122.1(1)° enclosed by the two terminal Cl atoms and a small angle enclosed by the two bridging Cl atoms of 89.8(1)°. The Ga-Cl bonds to the bridging chlorine atoms are longer than those to the terminal Cl atoms. Cl3 is involved in weak intermolecular contacts and thus exhibits a slightly longer Ga-Cl3 bond [2.112(1) Å] as

Table 2. Selected bond lengths [Å] and angles [°] of methyl-gallium dichloride.

	XRD (this work)	XRD (Lit. [11])	GED (Lit. [12])
Ga-C	1.921(3)	1.928(7)	1.949(7)
Ga-Cl1	2.331(1)	2.332(1)	2.339(3)
Ga-Cl1'	2.327(1)	2.327(1)	
Ga-Cl2	2.151(1)	2.155(2)	2.129(3)
C-Ga-Cl1	112.6(1)	112.6(1)	108.0(13)
C-Ga-Cl1'	113.7(1)	113.2(2)	
C-Ga-Cl2	127.1(1)	127.0(3)	131(3)
Ga-Cl1-Ga'	90.9(1)	91.1(1)	89.6(6)
Cl1-Ga-Cl1'	89.1(1)	88.9(1)	90.4(6)
Cl1-Ga-Cl1	103.5(1)	103.8(1)	106.3(6)

Fig. 2. Crystal structure and cell of $(MeGaCl_2)_2$. The dashed lines represent the shortest intermolecular Ga···Cl contacts.

compared to Ga-Cl4 [2.091(1) Å] with Cl4 being not involved in secondary bonding.

Crystal structure of methylgallium dichloride

In a recent publication on the structure on methyl-gallium dichloride Carmalt and coworkers report this compound to crystallize in the monoclinic crystal system, space group $C2/m$ [a, b, c, β: 11.999(2), 6.737(1), 7.218(1) Å, 126.20(1)°, $V = 470.8(1)$ Å^3] [9]. In our hands methylgallium dichloride crystallized in the monoclinic space group $C2/c$ with eight formula units in a cell (Fig. 2) with more than double the cell volume and significantly different cell dimensions [a, b, c, β: 11.7160(3), 6.9073(2), 12.5381(4) Å, 110.4326(13)°, $V = 950.82(5)$ Å^3]. The sample was prepared from dimethylgallium chloride and gallium trichloride. Crystals suitable for structure determination were obtained by crystallization from pentane

at ambient temperature. Structural parameter values of our new structure are listed in Table 2 together with those obtained by Carmalt *et al.* and the values from a gas phase structure determination by electron diffraction experiments [10]. The overall quality of our structure refinement is substantially better than that achieved in the earlier report.

As in Carmalt's structure, the primary aggregation of $MeGaCl_2$ is into dimers forming an almost square Ga_2Cl_2 ring with two terminal Cl atoms being *trans* oriented. This is consistent with the results from the gas phase. In the solid state the Ga-C bond is slightly shorter [1.921(3) Å] than in the gas phase [1.911(1) Å] but shorter than in solid trimethylgallium [1.975 Å on average, see below]. At 2.327(1) and 2.331(1) Å the distances Ga-Cl to the bridging Cl atoms are close to those found in the gas phase [2.229(3) Å] and expectedly shorter than in dimethylgallium chloride (vide infra), as the bridging atoms are not involved in secondary bonding as in Me_2GaCl.

However, the terminal Cl atoms are involved in secondary bonding making contacts to gallium atoms of neighbouring molecules. This leads to the formation of a stair-like layer structure (Fig. 2), as the secondary bonds lead to Ga_2Cl_2 four-membered ring units with long Ga···Cl contacts of 3.764 and 3.689 Å, which can only occur on opposite sides of the dimers due to the *trans* orientation of the Cl substituents. The aggregation mode is thus the same as for $(GaCl_3)_2$ (Fig. 1). The resulting total coordination number for the gallium atoms is (4+2). The primary coordination sphere of gallium is still four-coordinate and is a strongly distorted tetrahedron. The angle C-Ga-Cl$_{terminal}$ is 127.1(1)° and seems therefore compressed with respect to the gas phase value of 131(3)°, but the large standard deviation of the gas phase value reflects a great deal of flexibility for this parameter in the free molecule. However, a substantial widening of the C-Ga-Cl$_{terminal}$ angle does not take place, as could be expected to be the result of the accommodation of the secondary contacts to two further chlorine atoms.

It should be noted that methylaluminium dichloride [11] and dichlororgallane [12] crystallize isomorphous to methylgallium dichloride.

Methylindium dichloride, however, crystallizes in the tetragonal system (space group $I\bar{4}$) and forms a ladder-like aggregate with one In-Cl unit involved in a double stranded ladder-type aggregation with a primary In-Cl bond length of 2.400(1) Å, and In···Cl contacts of 3.203(2) and 3.799(3) Å

Table 3. Selected bond lengths [Å] and angles [°] of dimethylmethylgallium chloride.

	XRD	GED		XRD	GED
Ga-C	1.933(7)	1.946(3)	Ga-Cl	2.403(2)	2.378
Ga-Cl'	2.412(2)				
C-Ga-C	139.4(4)	132.1(27)	C-Ga-Cl	104.3(2)	
Cl-Ga-Cl'	89.2(1)	92.0	Ga-Cl-Ga'	90.4(1)	88.0
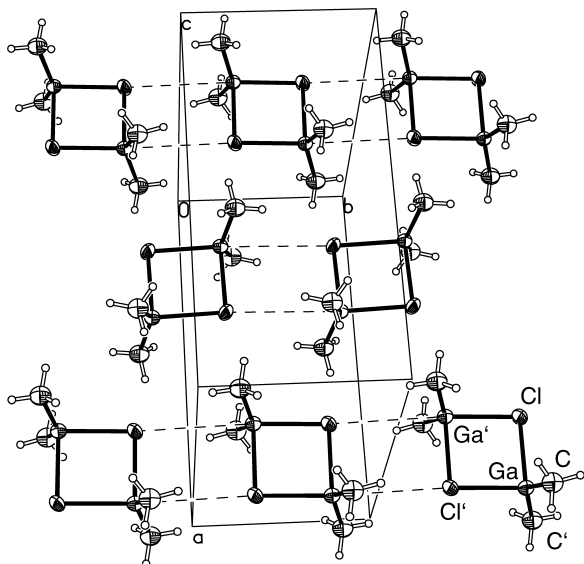
Fig. 3. Crystal structure and cell of $(Me_2GaCl)_2$. The dashed lines represent the shortest intermolecular Ga$\cdots$Cl contacts.

[13]. The indium atoms adopt a trigonal bipyramidal coordination geometry, *i.e.* the dimeric units of $MeInCl_2$ are strongly asymmetric but compensate this by stronger intermolecular interactions as compared to $MeGaCl_2$.

Crystal structure of dimethylgallium chloride

Dimethylgallium chloride was prepared by a ligand redistribution reaction from gallium chloride and trimethylgallium [14]. Within a few days of storage at ambient temperature in a Schlenk tube, sublimation afforded colourless crystals suitable for crystal structure determination. They belong to the orthorhombic space group *Ibam* with eight formula units in the cell. In the crystal two molecules of Me_2GaCl form centrosymmetric dimers, bridged by two chlorine atoms (Fig. 3). The same structure was found for this compound in the gas phase [15]. The central Ga_2Cl_2 four-membered ring is planar with valence angles of $89.2(6)°$ at the gallium atom and of $90.8(6)°$ at the chlorine atoms. The Ga-C bonds are shorter in the crystal [1.933(7) Å] than in the gas phase [1.946(3) Å], but they are also shorter than in crystalline trimethylgallium [1.957(1) Å, vide infra]. The two different Ga-Cl bonds [2.403(2) and 2.412(2) Å] are so similar that it is difficult on this basis to clearly identify the monomers. They are also very close to those in the related methyl-tris(trimethylsilyl)silyl-gallium chloride [2.406 and 2.420 Å] [16]. In contrast to the Ga-C bonds, the Ga-Cl bonds are longer in the solid state than in the gas phase [2.378(4) Å]. This might be attributed to the aggregation of the Ga_2Cl_2 four-membered rings into endless ladder-like band structures (Fig. 3). The intermolecular Ga$\cdots$Cl contacts have a length of 3.766 Å. This is a borderline value for what can still be regarded as a weakly attractive contact. The argument in favour of a contact is the correct orientation of positively and negatively polarized atoms. The distance of 3.766 Å is close to or even longer than the sum of the van der Waals radii, but it can be questioned, whether these tabulated data are really meaningful. A value of 1.87 Å found *e. g.* in ref. [17] surprisingly is substantially smaller than that of Al at 2.05 Å found in a different source of information [18]. The sums of van der Waals radii for Ga and Cl (for which also very different values exist) calculated on this basis and are between 3.62 and 3.80 Å.

On the basis of these weak intermolecular Ga$\cdots$Cl interactions, it may be rationalized why the Ga-Cl bonds orientated along the band direction are slightly longer (*trans* to the Ga$\cdots$Cl contacts) than those oriented perpendicular. The gallium atoms are (4+1) coordinate, but the intermolecular Ga$\cdots$Cl contact is too weak to lead to a significant distortion of the structure of the $(Me_2GaCl)_2$ dimers, as can bee seen from the C-Ga-Cl angles which are all equal. However, there is a significant difference between gas phase and solid state in the C-Ga-C angle [solid: $139.4(4)°$, gas $132.1(27)°$]. The Ga$\cdots$Cl distances between the bands of aggregation are 3.988 Å and thus out of the sum of the van der Waals radii.

The solid state structure of the indium analogue Me_2InCl [19] shows structural features similar to those of Me_2GaCl. However, in the indium compound one finds centrosymmetric but not square In_2Cl_2 rings aggregated into ladder-like bands (aggregation type D in Scheme 1). All In-Cl distances along the band direction are almost of equal length [2.945(6) and 2.954(6) Å], *i. e.* the identity of an $(Me_2InCl)_2$ dimer has nearly vanished. Furthermore the In$\cdots$Cl distances between the bands [3.450(9) Å] are only 0.5 Å longer

Table 4. Selected bond lengths [Å] and angles [°] of trimethylmethylgallium in the tetragonal crystals and in the gas phase [21].

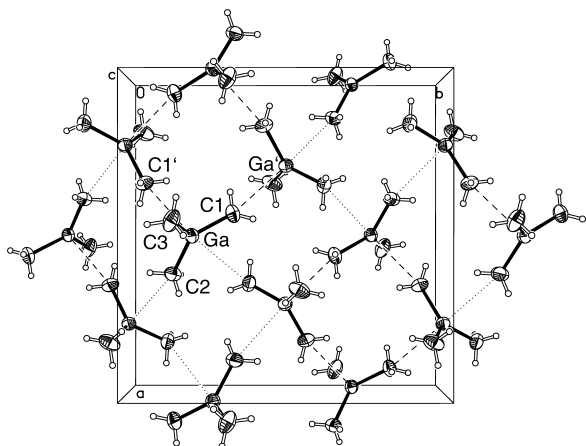|	XRD	GED		XRD	GED
Ga-C1	1.962(2)	1.967(2)	Ga-C2	1.958(3)	
Ga-C3	1.952(3)				
C1-Ga-C2	118.9(1)	118.6(4)	C1-Ga-C3	119.7(1)	
C2-Ga-C3	121.3(1)				
Ga···C1'	3.149(2)	Ga···C2'		3.647(2)	

Fig. 4. Crystal structure and tetragonal cell of GaMe₃. The dashed lines represent the aggregation of four GaMe₃ molecules into pseudo-tetramers, the dotted lines indicate the aggregation between these pseudo-tetramers.

than those within the bands and not as different as in Me₂GaCl where the difference between the Ga-Cl bonds and the loose intermolecular contacts is more than 1.3 Å. The total coordination number of six for the indium compound shows again that the differences between the structures of Me₂InCl and Me₂GaCl are the result of a greater tendency of indium atoms to adopt higher coordination numbers.

The crystal structure of Me₂AlCl is so far unknown and our own attempts failed since the compound tends to solidify as a glass, although the literature quotes even two melting points in the same publication for this compound [20].

Crystal structure of trimethylgallium

Although trimethylgallium is the basic unit of organogallium chemistry, it took until the year 2002 to determine its crystal structure [4]. The gas phase structure, however, was determined as early as 1974 [21]. Solid state structural studies were undertaken simultaneously and independently by two groups. Interestingly it was found that GaMe₃ crystallizes in a

monoclinic modification of low density (space group $C2/c$, $d = 1.444$ g cm^{-3} at -143 °C, two independent molecules) in the hands of Boese, Parsons and their co-workers [22], who applied a steep temperature gradient during crystallisation using an infrared laser driven microscale zone melting procedure. By contrast, a crystal of GaMe₃ in a tetragonal modification with a higher density was grown by us ($d = 1.453$ g cm^{-3} at -140 °C, space group $P4_2/n$), by establishing a solid liquid equilibrium at the melting point and carefully selecting a seed crystal, which was then allowed to grow very slowly by a slight reduction of temperature.

The structures of the trimethyl compounds of the other group 13 elements [23] are described in the literature. BMe₃ was only recently crystallised and its structure elucidated by Boese *et al.* [21]. It is monomeric, while AlMe₃ crystallises as a dimer with two bridging methyl units with short Al-C distances and four-coordinate Al atoms [24, 25], and InMe₃ [26] and TlMe₃ [27] are aggregated into tetramers with long intermolecular metal-carbon distances and the metal atoms adopting a primary trigonal planar coordination. There are also weaker interactions which connect the tetramers into layers. These structures of InMe₃ and TlMe₃ are closely related to the tetragonal structure of GaMe₃, which is shown in Fig. 4.

It can be described as consisting of GaMe₃ molecules with planar GaC₃ units (sum of angles about Ga 359.9°) which are aggregated into tetramers by weakly coordinating a methyl group of a neighbouring molecule to the electron deficient Ga centre. This methyl group estabilshes Ga···H distances of 2.95 to 2.96 Å, with the corresponding Ga···C distance at 3.149 Å. Although indium has a larger atomic radius than gallium, the corresponding distances in InMe₃ [In···C 3.083(12) Å] are shorter, but in TlMe₃ they are longer than in GaMe₃ (Tl···C 3.16 Å).

The tetrameric primary aggregates of GaMe₃ are connected to an endless two-dimensional network by further interactions between methyl groups and gallium atoms of other teramers, whereby the interactions are longer than those within the teramers [3.647(3) Å]. Again the respective distances in InMe₃ [In···C 3.558(15) Å] and also those in TlMe₃ [Tl···C 3.31 Å] are shorter.

The three Ga-C bonds of the GaMe₃ molecule in the *tetragonal* structure are different in length. Each primary Ga-C distance seems to depend on the lengths of the corresponding secondary Ga···C interactions: the shorter these interactions are, the longer is the Ga-C
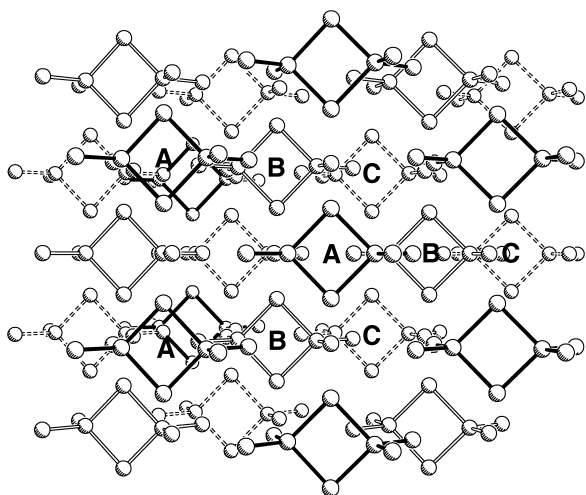
Fig. 5. Part of the pseudo cubic close-packed array of Ga_2Cl_6 molecules showing the ABC sequence of layers.

bond in the monomer: Ga-C(3) 1.952(3) Å (no Ga···C contact), Ga-C(2) 1.958(2) Å [long Ga···C(2)' contact of 3.647(2) Å] and Ga-C(1) 1.962(2) Å [short Ga···C(1)' contact of 3.149(2) Å]. Notably, the difference of the Ga-C bond length between gaseous {1.967(2) Å [21]} and solid GaMe$_3$ is very small, which indicates the weakness of the intermolecular interactions.

The *monoclinic* structure of GaMe$_3$ [22] can be described as a pseudo-polymer with Ga···C contacts of 3.096(3), 3.204 and 3.226 Å in length. Plane wave density functional theory calculations of Morrison on the two polymorphs of GaMe$_3$ [22] showed the tetragonal structure to be the ground state and the monoclinic one to be 3.6 kJ mol^{-1} higher in energy.

The nature of the Ga···C secondary interactions have been modelled by calculations on an isolated pair of GaMe$_3$ molecules on the MP2/TZVP level of theory which gave a distance of the Ga···C bridging of 3.206 Å with an interaction energy of 11.4 kJ mol^{-1}, which is in the range of a weak hydrogen bond [4]. This interaction energy was partitioned into 3.4 kJ mol^{-1} of electrostatic forces, 7.5 kJ mol^{-1} of a dispersion interaction and 4.2 kJ mol^{-1} of an ionic correlation contribution. A negative repulsive term of 3.8 kJ mol^{-1} was also found.

Conclusion

The crystal structures of gallium trichloride, methyl-gallium dichloride, dimethylgalllium chloride and trimethylgallium are illustrative examples for the

Table 5. Crystallographic data for GaCl$_3$, MeGaCl$_2$, Me$_2$GaCl and GaMe$_3$.

Compound	GaCl$_3$	MeGaCl$_2$	Me$_2$GaCl	GaMe$_3$
Formula	GaCl$_3$	CH$_3$GaCl$_2$	C$_2$H$_6$GaCl	C$_3$H$_9$Ga
Crystal system	monoclinic	monoclinic	orthorhombic	tetragonal
Space group	*C2/m*	*C2/c*	*Ibam*	*P4$_2$/n*
a [Å]	11.9152(5)	11.7160(3)	12.6641(12)	12.9532(3)
b [Å]	6.8128(4)	6.9073(2)	6.1751(4)	12.9532(3)
c [Å]	7.0258(3)	12.5381(4)	12.6513(11)	6.2588(1)
β [deg]	125.749(3)	110.4326(13)	90	90
V [Å^3]	462.87(4)	950.82(5)	989.36(14)	1050.13(4)
Z	4	8	8	8
M_r	176.07	155.65	135.24	114.82
T [K]	143(2)	143(2)	153(2)	143(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
D_{calc} [g cm^{-3}]	2.527	2.175	1.816	1.453
μ [mm^{-1}]	7.461	6.705	5.907	5.059
$R_1(F_o^2)^a$	0.0242	0.0286	0.0666	0.0336
$wR_2(F_o^2)$	0.0546	0.0623	0.1808	0.0882
CCDC-No.	226821	226820	226819	163478

[a] $(F_o > 4\sigma(F_o))$. $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2\}/\Sigma w(F_o^2)^2\}^{1/2}$.
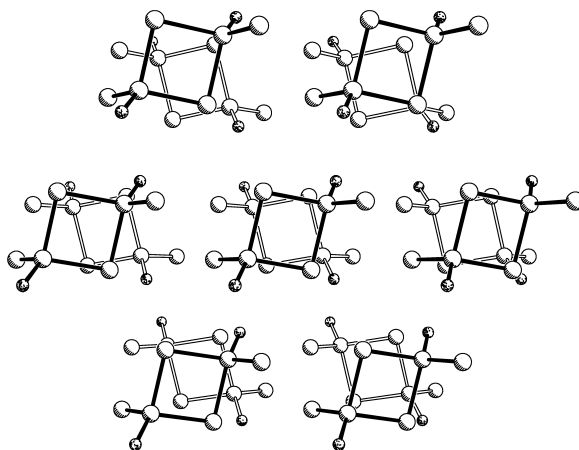

Fig. 6. Packing of the molecules of (MeGaCl$_2$)$_2$ showing the ABAB sequence of layers. The molecules with the solid lines represent the A layer, those drawn with open lines the B layer. Molecules of the A and B layers have different orientations of their Ga$_2$Cl$_2$ planes. Hydrogen atoms are omitted.

small structural differences between free reference molecules and those incorporated in crystals, where they get weakly aggregated and slightly deformed. Replacement of Cl atoms by methyl groups in the gallium chlorides of the general formula Me$_x$GaCl$_{3-x}$ leads to a reduction in the intermolecular contacts between the molecular dimeric units comprising four-membered Ga$_2$Cl$_2$ rings. (GaCl$_3$)$_2$ and (MeGaCl$_2$)$_2$ are aggregated into layers by the same aggregation type whereby each dimer is connected to four neigh-

bouring dimers *via* eight intermolecular Ga···Cl contacts. $(Me_2GaCl)_2$ is aggregated into a ladder-like structure whereby each molecule is connected to two neighbouring molecules *via* four intermolecular Ga···Cl contacts. None of the methyl gallium chlorides $(MeGaCl_2)_2$ and $(Me_2GaCl)_2$ uses Ga···C contacts for aggregation of the molecules. Only $GaMe_3$ aggregates itself into Ga···C bound pseudo-tetramers which are further aggregated into layers by even longer Ga···C contacts.

The motif of pseudo cubic close-packing, which was found in the structure of $(MeGaCl_2)_2$ by Carmalt *et al.* [9], is also suitable to describe our structure of $(GaCl_3)_2$, as is illustrated in Fig. 5. The relationship between these two structures is also obvious from the fact that both structures have the same space group ($C2/m$) and from the close similarity of the cell dimensions [a, b, c, β: $(GaCl_3)_2$ 11.9152(5), 6.8128(4), 7.0258(3) Å, 125.749(3)°; $(MeGaCl_2)_2$ [9] 11.999(2), 6.737(1), 7.218(1) Å, 126.20(1)°]. In contrast, our new structure of $(MeGaCl_2)_2$ shows a different kind of packing with an ABAB sequence of layers (see Fig. 6), whereby the molecules in the A and B layers have different orientations. This structure represents a second polymorph of $(MeGaCl_2)_2$.

Experimental Section

Crystal structure determinations

Suitable single crystals of $GaCl_3$, $MeGaCl_2$ and Me_2GaCl were selected under perfluoropolyether oil and mounted in a drop of it on the tip of a glass fibre. A crystal of $GaMe_3$ was grown from the melt sealed in a thin walled Duran glass capillary. Scattering intensities were collected on a Nonius DIP 2020 diffractometer. Structure solutions and refinements were undertaken with the program SHELXTL 5.01. Further details are listed in Table 5.

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