

Synthesis and purification of trimethylgallium for MOCVD: molecular structure of $(\text{KF})_4 \cdot 4(\text{Me}_3\text{Ga})^\dagger$

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Trimethylgallium was obtained from a 3:1 molar mixture of Me_2AlCl (1) and GaCl_3 (2) only in the presence of NaCl . The mechanism of the reaction was traced. It is postulated that the gallium–aluminium dimers $\text{Cl}_n\text{Me}_{2-n}\text{AlCl}_2\text{GaCl}_m\text{Me}_{2-m}$ (m and $n = 0, 1$ or 2), formed in consecutive alkylation steps, do not participate in further alkyl–chlorine exchange. NaCl splits the dimers that form the precipitate of $\text{Na}[\text{MeAlCl}_3]$ (3), thus liberating $\text{Me}_n\text{GaCl}_{3-n}$ which, on further alkylation by Me_2AlCl , finally yields Me_3Ga . For an MOCVD application, it is purified through a complex with KF , which under vacuum decomposes at $180\text{--}300^\circ\text{C}$, to yield a product contaminated by less than 1 ppm of the total impurities. The X-ray study of the complex reveals a tetrameric, highly symmetrical heterocubane of formula $(\text{KF})_4 \cdot 4(\text{Me}_3\text{Ga})$. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: methylgallium compounds; methylaluminium compounds; MOCVD; alkylation; X-ray structure

INTRODUCTION

The main, if not the single, industrial application of organogallium compounds is the production of epitaxial layers of III/V semiconductors. For two decades there has been a constant growth of demand for such compounds as precursors for the metallorganic chemical vapour deposition (MOCVD) technique. The growth proceeds in

parallel with the increase in the numbers of papers and patents appearing, as well as in the numbers of reviews and books¹ that summarize the present knowledge of synthesis, properties and applications of gallium organometallics.

Four basic routes for their preparation are described: (1) reaction of gallium with organomercury or organolead compounds; (2) metathesis between gallium halides and metal alkyls; (3) reaction of gallium alloys (Ga/Mg) or gallium vapour² with alkyl halides; (4) electrochemical methods of synthesis.³

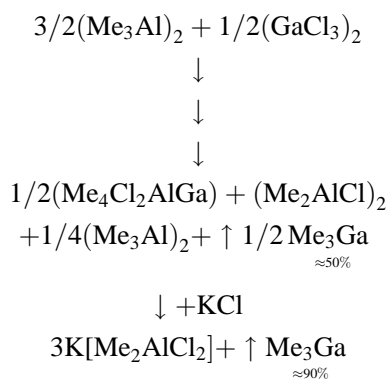
Generally, metathesis reactions are widely applied, but they have strong limitations. Attempts to exchange all of the alkyl groups of $\text{R}_m\text{M}'$ with MX_n to obtain R_nM failed in most cases. For example, in the case of R_3Ga synthesis the use of R_3Al results in exchange of even less than one alkyl group of trialkylaluminium in the reaction with GaCl_3 .^{3–5} Many reactions yield only partly alkylated R_mMX_p . When less alkylated organometallics were used for alkylation of MX_n the results were usually positive in only a few cases. They led mainly to R_mMX_p . The use of a complexing agent for the dealkylated aluminium compounds, in the reaction with BCl_3 or HgX_2 , results in the consumption of all the alkyl groups connected to aluminium. It has been explained that the complexation leads to a disproportionation with the formation of reactive R_3Al .

One of the metathetic methods for the synthesis of Me_3Ga is based on the reaction of GaCl_3 with a large excess of Me_3Al (Scheme 1). However, the yield of Me_3Ga is relatively low (approximately 50%). The calculations of the exchange reactions in the $(\text{Me}_3\text{Al})_2 + (\text{GaCl}_3)_2$ system performed by Fukin *et al.* show the presence of mixed dimers of formula $\text{Me}_n\text{Cl}_{6-n}\text{AlGa}$ ($n = 1\text{--}4$).⁶ It has been found that their concentration and composition depend on the molar ratio of the reagents. We suggest that mixed dimers $\text{Me}_n\text{Cl}_{6-n}\text{AlGa}$, formed in few reaction steps, deactivate the consecutive

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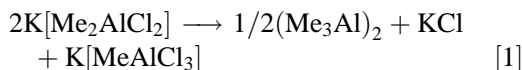


Scheme 1

reactions. Only a great excess of very reactive $(\text{Me}_3\text{Al})_2$ makes it possible to obtain a limited amount of the final product. First, the addition of KCl improved the yield to about 90% due to the splitting of both dimers with the formation of ionic complex $\text{K}[\text{Me}_2\text{AlCl}_2]$.

The corresponding reaction (also strongly exothermic) of $3\text{Me}_3\text{Al}$ with GaBr_3 yields a nearly stoichiometric amount of Me_3Ga .⁷ It seems that the weaker Br bridges $[117 \text{ kJ}(\text{mol Al—Br})^{-1}]$ compared with $132 \text{ kJ}(\text{mol Al—Cl})^{-1}$ in $(\text{AlX}_3)_2$ ⁸ in mixed dimers, if even they are formed, split easily during alkylation.

The suggestion that the inactive $\text{K}[\text{Me}_2\text{AlCl}_2]$ complex disproportionates via Eqn [1] to reproduce the reactive trimethylaluminium, does not agree with our earlier investigations, which indicated that the reaction is slow, also forming the $\text{K}[\text{Me}_3\text{AlCl}]$ complex which splits slowly only at elevated temperature to yield trimethylaluminium (K. B. Starowieyski, unpublished results).



For application in the MOCVD technique the method of purification to a level of not more than 1 ppm of the total amount of impurities (puratronic grade) is no less important than the effective synthetic methods. The conventional distillation methods have proved to be ineffective in removing the contamination (such as silicon compounds hydrocarbons or oxidized organometallics of the R_2MOR type) to the level demanded.^{9–11} A major advance in obtaining the puratronic organometallic precursors has been the application of the adduct

purification techniques. The principle of the method is to form, from an organometallic with an organic base that is of very low volatility and that is stable at room temperature, a complex which at elevated temperature exists in equilibrium with the substrates. The crystalline complex precipitating from the solution is filtered, washed with petroleum ether, dried under vacuum, then decomposed under vacuum at a higher temperature. The resulting R_3M is electronically pure.^{9,12,13} Though the method seems elegant, there are also some disadvantages, like the high price of the organic donors and darkening of the base during the process, which as a consequence demands the purification of the donor used.

The aim of this investigation was to find an effective method of synthesis and a better method of purification of R_3Ga , using simple chemical reactions and cheap reactants. The determination of the intermediate compounds was expected to help in understanding the mechanism of transalkylation and, as a result, could help to optimize the process.

EXPERIMENTAL

Synthesis of Me_3Ga :^{14a}

Trimethylgallium was obtained in a strongly exothermic reaction of GaCl_3 with $3\text{Me}_2\text{AlCl}$ in the presence of 3NaCl . A 750-ml three-necked flask equipped with thermometer, mechanical stirrer, dropping funnel and distillation set (Vigreux column, air and dry-ice condensers, collecting flask) was evacuated and filled with 5N (99.999% N_2) nitrogen. To the flask were added 1.52 mol of NaCl and 0.5 mol of liquid (warmed) GaCl_3 . To the contents in the flask, heated to 65°C and stirred, 1.51 mol of Me_2AlCl was added dropwise from a funnel. Me_3Ga began to distill slowly after more than half of dimethylaluminium chloride had been added. The rate of addition of Me_2AlCl was controlled at the beginning by the rise in temperature ($<70^\circ\text{C}$), and finally by the amount of Me_3Ga condensed. After having added all the Me_2AlCl , the reaction mixture was heated slowly to 150°C , to distill off the residual Me_3Ga . Vacuum was applied to increase the yield. This distillate was collected in a second container. In the fraction obtained under atmospheric pressure there was about 1% of organoaluminium compounds. The fraction was rectified on a 700-mm Dufton column and the product was collected at $56-58^\circ\text{C}$. The residue,

together with the vacuum distillate, was used in the consecutive reaction. The yield of Me_3Ga (calculated with respect to the gallium introduced into the reaction) after distillation was about 80% and the purity of the product was 99.9%.

Final purification of $\text{Me}_3\text{Ga}^{14b,c}$

A two-necked flask (11) was equipped with a dropping funnel and connected, through a Dufton column to a sintered glass filter, with a dry ice trap and closed by a bubbler connected with a nitrogen compensator. This assembly was evacuated and filled with 6N nitrogen. Finely ground and vacuum-dried (at 300 °C) KF (1.2 mol) and 200 ml of xylene, freshly distilled from a K/Na-benzophenone system, were placed in the flask. The dropping funnel was filled with 1 mol of Me_3Ga , which was then added dropwise to the flask. The mixture was refluxed for 24 h to complete the formation of the complex. After cooling, nice crystals were formed mainly on the walls of the flask. Xylene was poured out and the complex was crystallized once more from 200 ml of fresh xylene, to get rid of uncomplexed impurities (e.g. Me_2Zn). After the solid had been washed with xylene the flask was connected to a high vacuum line, through a Dufton column, sintered glass filter and liquid-nitrogen-cooled trap. The whole assembly was evacuated to about 10^{-6} mm Hg, and the flask was heated to about 130 °C (slow decomposition of the complex was observed). The vapour was collected as long as they contained traces of xylene. Then the content of the trap was vacuum-transferred to the predistillate container, connected to the line. The temperature of the complex was slowly raised to above 250 °C and pure Me_3Ga was collected in the trap. After 8 h more than 85% of the Me_3Ga introduced was recovered. Finally, the product was twice vacuum-transported to other containers on the line. To get rid of possible residual trace impurities, the initial ~1% was taken off and the last ~2%, possibly containing some heavy impurities, was left in the containers after each transportation. Both were finally transferred to the predistillate.

Trace analysis of $\text{Me}_3\text{Ga}^{15}$

An analysis was performed by microwave-induced plasma emission spectroscopy using an MIP-2 microwave generator (MIP-AES) equipped with a TE₁₀₁ rectangular cavity (Plasmatronika Service, Wrocław, Poland).

Me_3Ga , contaminated with volatile impurities, was introduced as a vapour into the plasma by argon or helium as a carrier gas, using the direct vapour sampling (DVS) technique. For this purpose, a laboratory-made DVS manifold was used, which consisted of a moisture trap and an oxygen scrubber (Hewlett-Packard), mass flow controller (Erg 1000 of DHN Ltd., Warszawa, Poland), sample vessel, and thermostated bath.

Volatile as well as non-volatile impurities were also analysed as aqueous solutions obtained after decomposition of the sample. Decomposition was performed in a petroleum ether solution by adding successively methyl alcohol, water and dilute nitric acid (15%). A previously described laboratory made nebulizer USN 1 was applied for the introduction of the aqueous solution. Argon and helium (99.998%) were used as plasma gases. The solvents and the reagents were of analytical reagent grade.

X-ray structure determination

Single crystals for the structural investigation of $(\text{KF})_4 \cdot 4(\text{Me}_3\text{Ga})$ were grown from a small sample according to the procedure described above, by slowly cooling a xylene solution of the complex. They are moisture- and oxygen-sensitive. A single crystal suitable for the X-ray diffraction studies was mounted on a goniometer head of a four-circle P3 (Siemens AG) diffractometer. The crystal class and the orientation matrix were obtained from the least-squares refinement of 25 reflections using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The intensities were collected in the ω - 2θ mode. The 751 measured intensities were corrected for Lorentz and polarization factors. An analytical absorption correction (Gaussian integration) was applied on the basis of the well-defined crystal shape. The structure was solved in P43m by direct methods using the *SHELXS-86*¹⁶ program. The full-matrix least-squares refinement method against F^2 values was carried out by means of the *SHELXL-97* program.¹⁷ All non-hydrogen atoms were refined with anisotropic displacement parameters. The methyl group bonded to Ga is disordered over two sites related by a crystallographic mirror plane with an s.o.f. of 50%. The H atoms were refined with fixed geometry, riding on their carrier atoms, with isotropic displacement parameters. The difference Fourier maps, calculated at a late stage of the refinement, showed no significant features. The weighting scheme used was $w^{-1} = \sigma^2 (F_o^2) + (0.0222P)^2$, where $P = 1/3 (F_o^2 + 2F_c^2)$. Selected

Table 1 Crystal data and structure refinement for (KF)₄·4(Me₃Ga)

Empirical formula	C ₁₂ H ₃₆ F ₄ Ga ₄ K ₄
Formula weight	691.69
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	P4̄3m
Unit cell dimensions	$a = b = c = 8.8695(9)$ Å
Volume	697.75(12) Å ³
Z	1
Density (calculated)	1.646 Mg m ⁻³
Absorption coefficient	4.438 mm ⁻¹
F(000)	344
Crystal size	0.39 × 0.26 × 0.17 mm ³
θ range for data collection	2.30 to 24.85 °
Index ranges	0 ≤ h ≤ 10, 0 ≤ k ≤ 10, 0 ≤ l ≤ 10
Reflections collected	751
Independent reflections	163 [R _{int} = 0.0306]
Completeness to θ = 24.85 °	100.0%
Absorption correction	Gaussian
Max. and min. transmission	0.4923 and 0.3323
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	163 / 0 / 23
Goodness-of-fit on F ²	1.115
Final R indices [I > 2σ(I)]	R1 = 0.0137, wR2 = 0.0337
R indices (all data)	R1 = 0.0139, wR2 = 0.0338
Absolute structure parameter	0.06(4)
Extinction coefficient	0.0087(15)
Largest diff. peak and hole	0.185 and -0.237 e Å ⁻³

crystallographic data, the parameters of data collection and the refinement procedures are presented in Table 1.

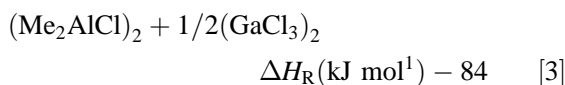
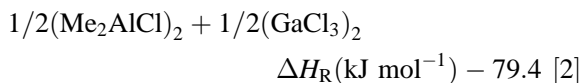
RESULTS AND DISCUSSION

Synthesis

The reaction of (Me₂AlCl)₂ (**1**) with (GaCl₃)₂ (**2**) was studied for various molar ratios of the reactants. It was found that the equimolar reaction of **1** with **2** is strongly exothermic (*vide infra*). Addition of further amounts of **1** did not cause a drastic increase of the exothermic effect. However, we failed to obtain Me₃Ga by this method, even when a tenfold molar excess of (Me₂AlCl)₂ was used. The distillation of the mixture obtained from the reaction of 1 mol of **2** and 10 mol of **1** began at 118 °C. The fraction obtained up to 128 °C gave a mixture composed of 82.3 mol% of **1** + MeAlCl₂ and 17.7 mol% of Me_nGaCl_{3-n} (n = 1 or 2), but not

even a trace of Me₃Ga. The dramatic increase in the yield of the reaction of (Me₃Al)₂ with **2** after addition of KCl may be explained by the splitting of the inactive mixed dimer (Me₄Cl₂AlGa) with formation of reactive Me₂GaCl and precipitation of the ionic complex K[Me₂AlCl₂].⁵ Expecting a similar effect, we added NaCl to the mixture of **1** with **2** to split the mixed dimers and to form Me_nGaCl_{3-n} able to undergo further alkylation. NaCl reacts selectively with MeAlCl₂ to precipitate Na[MeAlCl₃] **3** but does not form complexes with Me₂AlCl. We have assumed that in order for the complexation of dealkylated MeAlCl₂ to run effectively, the reaction should be carried out at an elevated temperature (65 °C). The formation of Me₃Ga in the reaction mixture was first observed after adding more than 60% of the required amount of **1**. The reason for the yield of trimethylgallium being lower than theoretical (around 80%) can be explained by the side reactions of NaCl with Me_nGaCl_{3-n} (n = 1, and perhaps 2) resulting in the precipitation of unreactive ionic complexes.

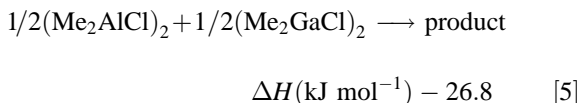
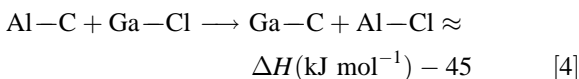
To understand better the mechanism of the method reported here for the synthesis of Me_3Ga , we have performed a thermochemical study of the interaction of Me_2AlCl with GaCl_3 . The equimolar reaction of **1** with **2** is strongly exothermic (Eqn [2]). A slightly larger effect was observed for the reaction in a 2:1 molar ratio (Eqn [3]).



These results demonstrate strongly that the excess of **1** does not effect further alkylation.

The double exchange of substituents (Eqn [4])¹⁸ is exothermic but the value, depending on the compounds used, is much smaller than that obtained in the reaction of **1** + **2**. Assuming that the exothermicity of the reaction of $\text{Me}_3\text{Ga} + (\text{GaCl}_3)_2$ ¹⁹ is mainly due to the formation of the Ga—Cl—Ga bridging bond, we can calculate the formation of one bridge as about -44 kJ mol^{-1} (compared with 60 kJ mol^{-1} for formation of the Al—Cl—Al bridge). Because the mixing represented by Eqn [5] does not produce Me_3Ga , it can be postulated that the energy evolved during the reaction²⁰ is predominantly due to the formation of two Ga—Cl—Al mixed bridges which should be more stable than the symmetrical bridges. Adding the heats of exchange of the substituents and of the mentioned formation of two Ga—Cl—Al mixed bridges, the sum is about 72 kJ mol^{-1} —close to the result measured for the mixing **1** with **2** in a ratio of

1:1.



Our attempts to isolate a definite product(s) from the equimolar reaction of **1** with **2** in toluene or CH_2Cl_2 failed. The product obtained after evaporation of the solvent gave low-melting crystals (ca 35°C) with a molar ratio of Al/Ga $\geq 1:1$. The molecular weight (283) is a little higher than calculated (269) for $\text{Cl}(\text{Me})\text{AlCl}_2\text{Ga}(\text{Me})\text{Cl}$ (**4**) [the result can be attributed also to a mixture of $(\text{MeAlCl}_2)_2$ (**5**) and $(\text{MeGaCl}_2)_2$ (**6**)]. Further recrystallization from toluene leads to a product with an increased gallium/aluminium ratio. These results suggest the presence of the equilibrium of Eqn [6] although shifted practically to the left.

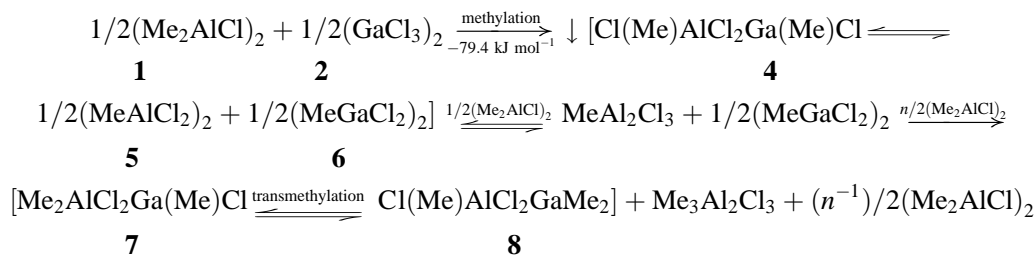


Presence of the solvent washed out the traces of **5**, due to the better solubility of MeAlCl_2 , to the extent that its X-ray structure shows only the existence of the poorly soluble dimeric $(\text{MeGaCl}_2)_2$.

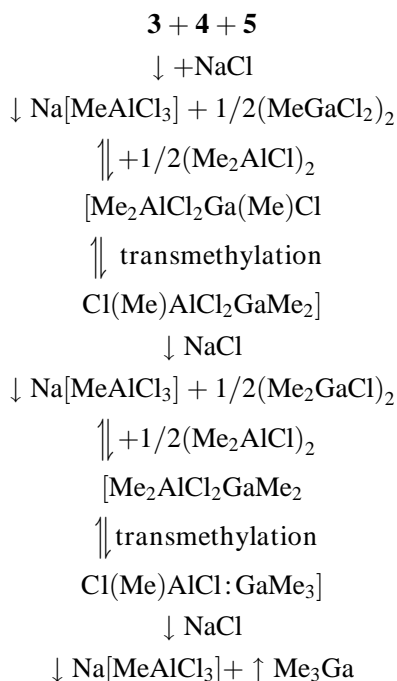
Based on the results discussed above we are proposing the mechanism of the reaction and its termination shown in scheme 2, and the composition of the final mixture of products and reactants.

The alkylation of **2** leads to the formation of a mixed dimer **4** which can exist in equilibrium with **5** and **6**, but shifted strongly to the left. Further addition of **1** terminates the reaction with the formation of a higher alkylated mixed dimer as well as of $\text{Me}_3\text{Al}_2\text{Cl}_3$.

Addition of NaCl (Scheme 3) to **4**, including also



Scheme 2



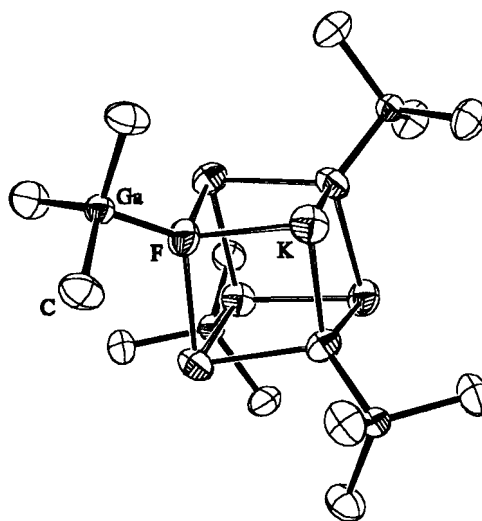
Scheme 3

some traces of **5** + **6**, results in the precipitation of **3** and liberation of **6**. Complex **6** reacts with the excess of Me_2AlCl to form a new dimer, composed of a mixture of two isomers, **7** and **8**. In the presence of NaCl the transmethylated form **8** splits with the precipitation of **3** and formation of Me_2GaCl . Introduction of a further amount of dimethylaluminium chloride results in the formation of a new mixed dimer **9** which, after transmethylation to **10**, can be split by NaCl finally to form Me_3Ga .

The proposed mechanism is supported by Me_3Ga evolution from the reaction mixture, first observed after addition of more than 60% of the required amount of Me_2AlCl . The yield of trimethylgallium, lower than theoretical (around 80%), can be explained by the side reactions of NaCl with $\text{Me}_n\text{GaCl}_{3-n}$ ($n=1$, and perhaps 2) resulting in the precipitation of unreactive ionic complexes.

Purification

The purification, according to our method, is realized by the formation of a complex of Me_3Ga with KF . The complex can be obtained in aromatic hydrocarbons (but not in aliphatic hydrocarbons!) boiling above 100°C . Chemisorption of Me_3Ga on bulk potassium fluoride weakens the surface lattice

Figure 1 Molecular structure of $(\text{KF})_4 \cdot 4(\text{Me}_3\text{Ga})$.

of $\text{K}-\text{F}$, shifting the negative charge on the fluorine anion towards Me_3Ga and enabling the neighbouring K^+ cations to interact with the π aromatic system of the solvent. That makes it possible to split off and dissolve the clusters of general formula $(\text{KF})_{x \cdot y}(\text{GaMe}_3) \cdot z(\text{ArMe})$ from the bulk $\text{KF} \cdot n(\text{GaMe}_3)$. They are rearranged to form crystals which appear to be complexed heterocubanes of formula $(\text{KF})_4 \cdot 4(\text{Me}_3\text{Ga})$ (Scheme 4; Fig. 1). The reaction, even when performed at the boiling temperature of the Me_3Ga -bulk KF -toluene mixture, is very slow because of the need to splitting off bulk KF (lattice energy of $\text{K}-\text{F}$ bond, -815 kJ mol^{-1}).²¹

Molecular structure

$\text{KF} \cdot \text{GaMe}_3$ was first synthesized by Wilson and Dehnicke.²² On the basis of IR/R investigations

Table 2 Selected bond lengths (Å) and angles ($^\circ$) for $(\text{KF})_4 \cdot 4(\text{Me}_3\text{Ga})$

Ga(1)-F(1)	1.954(3)
Ga(1)-C(1)	1.986(5)
Ga(1)-K(1)	3.983(7)
K(1)-F(1)	2.644(2)
F(1)-Ga(1)-C(1)	103.59(16)
F(1)-K(1)-F(1) ^a	81.22(11)
Ga(1)-F(1)-K(1)	119.26(7)

^a Symmetry transformations used to generate equivalent atoms marked by prime ($'$). $-x + 1, y, -z + 1$

they have proposed a polymeric structure for the anion, with linear Ga–F–Ga bridges, of formula $[-\text{Ga}(\text{Et}_3)-\text{F}-]_n^{n-}$ with D_{3h} symmetry. For the potassium salt Dötzer²³ later proposed an ionic complex structure.

As found by X-ray crystallographic studies, $\text{KF}\cdot\text{GaMe}_3$ forms tetrameric molecular with a cubic core^{24–26} crystallizing in the cubic space group $P43m$. The molecular structure of the complex is shown in Fig. 1. Selected bond lengths and bond angles are presented in Table 2. The main structural feature is a slightly distorted ionic K_4F_4 heterocubane central core, which is comparable topologically with a structural fragment observed in crystalline KF . The K–F distances are equal [2.644(2) Å] and are comparable with the value of 2.672 Å for KF .²² The distortion of the K_4F_4 heterocubane core can be characterized as outward movements of potassium cations along the cube space diagonals, which leads to the formation of butterfly-like cubic faces with torsion angles of K–F–F–K = 168.8(1)°. The methyl groups of Me_3Ga shield the ionic centre of the tetrameric molecule. The Ga atoms possess distorted tetrahedral coordination of C_3GaF with the C–Ga–C and C–Ga–F angles of 114.7(1)° and 103.6(2)° respectively. The Ga–F distance [1.954(3) Å] is somewhat shorter than the bond length [1.970(4) Å] observed in a similar compound, $[\text{CsFGa}(\text{iPr})_3]_4$.²⁴ The arrangement of the methyl groups around the potassium cations with a relatively short K...C distance of 3.455(5) Å indicates weak intermolecular interactions of partly ionic character.

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