

(KF)₄·4GaMe₃

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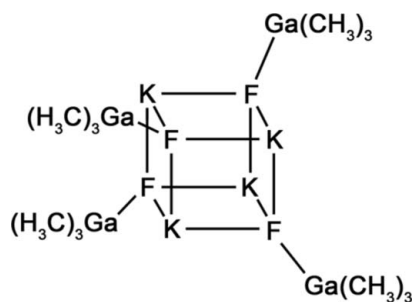
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 Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(K-F) = 0.001$ Å; R factor = 0.014; wR factor = 0.035; data-to-parameter ratio = 21.6.

In the structure of tetrakis(potassium fluoridotrimethylgallium), or tetra- μ_4 -fluorido-dodecamethyltetrapotassium-tetragallium, (KF)₄·4Ga(CH₃)₃ or [K₄Ga₄(CH₃)₁₂F₄], the F atoms of the K₄F₄ cube coordinate to the Ga(CH₃)₃ groups. The crystallographic site symmetry of the tetramer is 23 (T).

Related literature

For related literature, see: Elschenbroich (2003); Pauer & Sheldrick (1993); Starowieyski *et al.* (2000); Weiss *et al.* (1970); Wilson & Dehnicke (1974).



Experimental

Crystal data

[K₄Ga₄(CH₃)₁₂F₄]
 $M_r = 691.69$
 Cubic, $F\bar{4}3c$
 $a = 17.760$ (2) Å
 $V = 5601.8$ (11) Å³

$Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 4.42$ mm⁻¹
 $T = 295$ (2) K
 $0.48 \times 0.40 \times 0.37$ mm

Data collection

Stoe IPDS 2T diffractometer
 Absorption correction: numerical
 (*X-RED*; Stoe & Cie, 2001)
 $T_{\min} = 0.225$, $T_{\max} = 0.292$

2577 measured reflections
 453 independent reflections
 376 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.014$
 $wR(F^2) = 0.035$
 $S = 1.10$
 453 reflections
 21 parameters
 H-atom parameters constrained

$\Delta\rho_{\max} = 0.13$ e Å⁻³
 $\Delta\rho_{\min} = -0.18$ e Å⁻³
 Absolute structure: Flack (1983),
 with 195 Friedel pairs
 Flack parameter: 0.02 (2)

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-----------------------|-------------|--------------------------|------------|
| K1—F1 | 2.6501 (10) | Ga1—C1 | 1.982 (2) |
| F1—Ga1 | 1.9528 (18) | | |
| F1—K1—F1 ⁱ | 81.31 (6) | F1—Ga1—C1 | 103.38 (8) |
| K1—F1—K1 ⁱ | 98.07 (5) | C1 ⁱⁱ —Ga1—C1 | 114.81 (6) |

 Symmetry codes: (i) $x, -y + 1, -z + 1$; (ii) z, x, y .

Data collection: *X-AREA* (Stoe & Cie, 2005); cell refinement: *X-AREA*; data reduction: *X-AREA* and *X-RED* (Stoe & Cie, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SF3049).

References

- Brandenburg, K. (1998). *DIAMOND*. Version 2.0. University of Bonn, Germany.
- Elschenbroich, C. (2003). *Organometallics*, 4th ed., pp. 123–124. Wiesbaden: Teubner.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Pauer, F. & Sheldrick, G. M. (1993). *Acta Cryst.* **C49**, 1283–1284.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Starowieyski, K. B., Chwojnowski, A., Jankowski, K., Lewinski, J. & Zachara, J. (2000). *Appl. Organomet. Chem.* **14**, 616–622.
- Stoe & Cie (2001). *X-RED*. Version 1.22. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (2005). *X-AREA*. Stoe & Cie, Darmstadt, Germany.
- Weiss, E., Hoffmann, K. & Gruetzmacher, H. F. (1970). *Chem. Ber.* **103**, 1190–1197.
- Wilson, I. L. & Dehnicke, K. (1974). *J. Organomet. Chem.* **67**, 229–235.

supplementary materials

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(KF)₄·4GaMe₃

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Comment

The potassium fluoride adduct (KF)₄·4GaMe₃, (1), is a suitable intermediate in the purification of GaMe₃, since this reactive compound can be liberated by simply heating (1) in vacuum (Starowieyski *et al.*, 2000). (1) crystallizes in space group $F\bar{4}3c$, $z = 8$. The K and F atoms in (1) form a heterocubane structure with the fluorine atoms coordinating to the gallium atoms of the Ga(CH₃)₃ groups. This extends the number of valence electrons of the gallium atoms from six to a complete octet and increases the stability significantly (Elschenbroich, 2003). The first report on the synthesis of the KF–Ga(CH₃)₃ complex appeared in 1974 (Wilson & Dehnicke, 1974). Originally the structure of (1) was reported in space group $P\bar{4}3m$, $z = 1$ (Starowieyski *et al.*, 2000). However, then the carbon atom of the refined methyl group occupies a general position resulting in disorder with half occupancy. Isostructural with (1) is the potassium silanolate [KOSi(CH₃)₃]₄, which also has originally been characterized by powder diffraction and described in space group $P\bar{4}3m$ (Weiss *et al.*, 1970); the structure analysis has been corrected after refinement in space group $F\bar{4}3c$ (Pauer & Sheldrick, 1993).

We observed reflections with non-integer Miller indices in (1), if indexing is based on the cubic primitive cell, and succeeded in refinement in space group $F\bar{4}3c$ with twice the lattice parameter a and without disorder of the methyl group. Similar to the isostructural potassium silanolate, these reflections were obviously not recognized in the original structure analysis. This is understandable, since only few reflections hkl with odd indices are allowed at low diffraction angles because of the zonal extinctions in $F\bar{4}3c$, that allow Miller indices hhl only for $h,l = 2n$. Therefore only two reflections with odd indices at 2Θ angles below 20° can be observed. A data set collected at 180 K gives the same results with lattice parameter $a = 17.608$ (2) Å and smaller thermal ellipsoids.

The unit cell of (1) contains eight formula units (KF)₄·4Ga(CH₃)₃ with the K, F and Ga atoms on the threefold axes. The K₄F₄ heterocubane shows K–F–K angles of 98.07 (5)°. The main difference to the description in $P\bar{4}3m$ is the well ordered arrangement of the methyl groups. Important geometric parameters of (1) are summarized in table 2.

Experimental

Ga(CH₃)₃ has been synthesized by reaction of GaCl₃ with methyl lithium in diethylether. (KF)₄·4Ga(CH₃)₃ was prepared by complexation with potassium fluoride in toluene similar to the procedure described by Starowieyski *et al.* (Starowieyski *et al.*, 2000).

Refinement

Structure solution and refinement: *SHELX97* (Sheldrick, 1997)

Figures

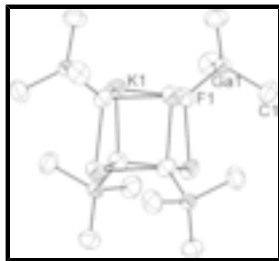


Fig. 1. Structure of $(\text{KF})_4 \cdot 4\text{Ga}(\text{CH}_3)_3$ showing 50% probability ellipsoids (hydrogen atoms omitted).

tetra- μ_4 -fluorido-dodecamethyltetrapotassiumtetragallium

Crystal data

$[\text{K}_4\text{Ga}_4(\text{CH}_3)_{12}\text{F}_4]$

$M_r = 691.69$

Cubic, $F\bar{4}3c$

Hall symbol: F -4c 2 3

$a = 17.760$ (2) Å

$b = 17.760$ (2) Å

$c = 17.760$ (2) Å

$\alpha = 90^\circ$

$\beta = 90^\circ$

$\gamma = 90^\circ$

$V = 5601.8$ (11) Å³

$Z = 8$

$F_{000} = 2752$

$D_x = 1.640$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 4321 reflections

$\theta = 2.0\text{--}29.6^\circ$

$\mu = 4.42$ mm⁻¹

$T = 295$ (2) K

Block, colorless

$0.48 \times 0.40 \times 0.37$ mm

Data collection

Stoe IPDS 2T
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: plane graphite

Detector resolution: 6.67 pixels mm⁻¹

$T = 295$ (2) K

rotation method, ω scans

Absorption correction: numerical
(X-RED; Stoe & Cie, 2001)

$T_{\min} = 0.225$, $T_{\max} = 0.292$

2577 measured reflections

453 independent reflections

376 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.045$

$\theta_{\max} = 25.9^\circ$

$\theta_{\min} = 2.3^\circ$

$h = -21 \rightarrow 21$

$k = -5 \rightarrow 19$

$l = -21 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.013P)^2 + 2.0232P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

| | |
|--|---|
| $R[F^2 > 2\sigma(F^2)] = 0.014$ | $(\Delta/\sigma)_{\max} = 0.002$ |
| $wR(F^2) = 0.035$ | $\Delta\rho_{\max} = 0.13 \text{ e } \text{\AA}^{-3}$ |
| $S = 1.10$ | $\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$ |
| 453 reflections | Extinction correction: SHELXL97 (Sheldrick, 1997), $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$ |
| 21 parameters | Extinction coefficient: 0.00081 (6) |
| Primary atom site location: structure-invariant direct methods | Absolute structure: Flack (1983), 195 Friedel pairs |
| Secondary atom site location: difference Fourier map | Flack parameter: 0.02 (2) |
| Hydrogen site location: inferred from neighbouring sites | |

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|---------------|---------------|---------------|----------------------------------|
| K1 | 0.57967 (2) | 0.57967 (2) | 0.42033 (2) | 0.0535 (2) |
| F1 | 0.56874 (6) | 0.56874 (6) | 0.56874 (6) | 0.0508 (5) |
| Ga1 | 0.632228 (10) | 0.632228 (10) | 0.632228 (10) | 0.03593 (14) |
| C1 | 0.62937 (17) | 0.58083 (14) | 0.73121 (12) | 0.0619 (6) |
| H1A | 0.5784 | 0.5672 | 0.7430 | 0.093* |
| H1B | 0.6484 | 0.6141 | 0.7693 | 0.093* |
| H1C | 0.6599 | 0.5363 | 0.7293 | 0.093* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|---------------|--------------|--------------|
| K1 | 0.0535 (2) | 0.0535 (2) | 0.0535 (2) | -0.00930 (18) | 0.00930 (18) | 0.00930 (18) |
| F1 | 0.0508 (5) | 0.0508 (5) | 0.0508 (5) | -0.0086 (5) | -0.0086 (5) | -0.0086 (5) |
| Ga1 | 0.03593 (14) | 0.03593 (14) | 0.03593 (14) | -0.00040 (7) | -0.00040 (7) | -0.00040 (7) |
| C1 | 0.0710 (17) | 0.0682 (15) | 0.0465 (13) | 0.0086 (14) | 0.0009 (13) | 0.0141 (11) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|---------------------|-------------|---------------------|-------------|
| K1—F1 | 2.6501 (10) | F1—Ga1 | 1.9528 (18) |
| K1—F1 ⁱ | 2.6502 (10) | F1—K1 ⁱ | 2.6502 (10) |
| K1—F1 ⁱⁱ | 2.6502 (10) | F1—K1 ⁱⁱ | 2.6502 (10) |

supplementary materials

| | | | |
|---|-------------|---|--------------|
| K1—C1 ⁱⁱⁱ | 3.473 (2) | Ga1—C1 ^{vii} | 1.982 (2) |
| K1—C1 ^{iv} | 3.473 (2) | Ga1—C1 ^{viii} | 1.982 (2) |
| K1—C1 ^v | 3.473 (2) | Ga1—C1 | 1.982 (2) |
| K1—Ga1 ⁱ | 3.9881 (6) | Ga1—K1 ⁱⁱ | 3.9882 (6) |
| K1—Ga1 ⁱⁱ | 3.9881 (5) | Ga1—K1 ⁱ | 3.9882 (5) |
| K1—Ga1 | 3.9881 (5) | C1—H1A | 0.96 |
| K1—K1 ⁱ | 4.0023 (13) | C1—H1B | 0.96 |
| K1—K1 ⁱⁱ | 4.0023 (13) | C1—H1C | 0.96 |
| K1—K1 ^{vi} | 4.0023 (13) | | |
| F1—K1—F1 ⁱ | 81.31 (6) | C1 ⁱⁱⁱ —K1—K1 ⁱⁱ | 100.60 (5) |
| F1—K1—F1 ⁱⁱ | 81.31 (6) | C1 ^{iv} —K1—K1 ⁱⁱ | 149.72 (5) |
| F1 ⁱ —K1—F1 ⁱⁱ | 81.31 (6) | C1 ^v —K1—K1 ⁱⁱ | 133.47 (4) |
| F1—K1—C1 ⁱⁱⁱ | 95.47 (5) | Ga1 ⁱ —K1—K1 ⁱⁱ | 109.327 (10) |
| F1 ⁱ —K1—C1 ⁱⁱⁱ | 168.81 (5) | Ga1 ⁱⁱ —K1—K1 ⁱⁱ | 59.882 (9) |
| F1 ⁱⁱ —K1—C1 ⁱⁱⁱ | 108.91 (6) | Ga1—K1—K1 ⁱⁱ | 59.884 (9) |
| F1—K1—C1 ^{iv} | 108.91 (6) | K1 ⁱ —K1—K1 ⁱⁱ | 60.0 |
| F1 ⁱ —K1—C1 ^{iv} | 95.47 (5) | F1—K1—K1 ^{vi} | 84.06 (4) |
| F1 ⁱⁱ —K1—C1 ^{iv} | 168.81 (5) | F1 ⁱ —K1—K1 ^{vi} | 40.97 (2) |
| C1 ⁱⁱⁱ —K1—C1 ^{iv} | 75.35 (7) | F1 ⁱⁱ —K1—K1 ^{vi} | 40.97 (2) |
| F1—K1—C1 ^v | 168.81 (5) | C1 ⁱⁱⁱ —K1—K1 ^{vi} | 149.72 (5) |
| F1 ⁱ —K1—C1 ^v | 108.91 (6) | C1 ^{iv} —K1—K1 ^{vi} | 133.47 (4) |
| F1 ⁱⁱ —K1—C1 ^v | 95.47 (5) | C1 ^v —K1—K1 ^{vi} | 100.60 (5) |
| C1 ⁱⁱⁱ —K1—C1 ^v | 75.35 (7) | Ga1 ⁱ —K1—K1 ^{vi} | 59.882 (9) |
| C1 ^{iv} —K1—C1 ^v | 75.34 (7) | Ga1 ⁱⁱ —K1—K1 ^{vi} | 59.882 (9) |
| F1—K1—Ga1 ⁱ | 100.42 (2) | Ga1—K1—K1 ^{vi} | 109.329 (11) |
| F1 ⁱ —K1—Ga1 ⁱ | 25.27 (3) | K1 ⁱ —K1—K1 ^{vi} | 60.0 |
| F1 ⁱⁱ —K1—Ga1 ⁱ | 100.42 (2) | K1 ⁱⁱ —K1—K1 ^{vi} | 60.0 |
| C1 ⁱⁱⁱ —K1—Ga1 ⁱ | 148.41 (5) | Ga1—F1—K1 | 119.32 (4) |
| C1 ^{iv} —K1—Ga1 ⁱ | 73.72 (4) | Ga1—F1—K1 ⁱ | 119.32 (4) |
| C1 ^v —K1—Ga1 ⁱ | 90.69 (5) | K1—F1—K1 ⁱ | 98.07 (5) |
| F1—K1—Ga1 ⁱⁱ | 100.42 (2) | Ga1—F1—K1 ⁱⁱ | 119.32 (4) |
| F1 ⁱ —K1—Ga1 ⁱⁱ | 100.42 (2) | K1—F1—K1 ⁱⁱ | 98.07 (5) |
| F1 ⁱⁱ —K1—Ga1 ⁱⁱ | 25.27 (3) | K1 ⁱ —F1—K1 ⁱⁱ | 98.06 (5) |
| C1 ⁱⁱⁱ —K1—Ga1 ⁱⁱ | 90.69 (5) | F1—Ga1—C1 ^{vii} | 103.38 (8) |
| C1 ^{iv} —K1—Ga1 ⁱⁱ | 148.41 (5) | F1—Ga1—C1 ^{viii} | 103.38 (8) |
| C1 ^v —K1—Ga1 ⁱⁱ | 73.72 (4) | C1 ^{vii} —Ga1—C1 ^{viii} | 114.82 (6) |
| Ga1 ⁱ —K1—Ga1 ⁱⁱ | 112.761 (9) | F1—Ga1—C1 | 103.38 (8) |
| F1—K1—Ga1 | 25.27 (3) | C1 ^{vii} —Ga1—C1 | 114.81 (6) |
| F1 ⁱ —K1—Ga1 | 100.42 (2) | C1 ^{viii} —Ga1—C1 | 114.81 (6) |
| F1 ⁱⁱ —K1—Ga1 | 100.42 (2) | F1—Ga1—K1 | 35.407 (11) |
| C1 ⁱⁱⁱ —K1—Ga1 | 73.72 (4) | C1 ^{vii} —Ga1—K1 | 76.52 (8) |

| | | | |
|---------------------------------------|--------------|--|-------------|
| C1 ^{iv} —K1—Ga1 | 90.69 (5) | C1 ^{viii} —Ga1—K1 | 94.34 (9) |
| C1 ^v —K1—Ga1 | 148.40 (5) | C1—Ga1—K1 | 136.33 (8) |
| Ga1 ⁱ —K1—Ga1 | 112.763 (9) | F1—Ga1—K1 ⁱⁱ | 35.408 (11) |
| Ga1 ⁱⁱ —K1—Ga1 | 112.763 (9) | C1 ^{vii} —Ga1—K1 ⁱⁱ | 136.33 (8) |
| F1—K1—K1 ⁱ | 40.97 (2) | C1 ^{viii} —Ga1—K1 ⁱⁱ | 76.52 (8) |
| F1 ⁱ —K1—K1 ⁱ | 40.97 (2) | C1—Ga1—K1 ⁱⁱ | 94.34 (9) |
| F1 ⁱⁱ —K1—K1 ⁱ | 84.06 (4) | K1—Ga1—K1 ⁱⁱ | 60.234 (17) |
| C1 ⁱⁱⁱ —K1—K1 ⁱ | 133.48 (4) | F1—Ga1—K1 ⁱ | 35.408 (11) |
| C1 ^{iv} —K1—K1 ⁱ | 100.60 (5) | C1 ^{vii} —Ga1—K1 ⁱ | 94.34 (9) |
| C1 ^v —K1—K1 ⁱ | 149.72 (5) | C1 ^{viii} —Ga1—K1 ⁱ | 136.33 (8) |
| Ga1 ⁱ —K1—K1 ⁱ | 59.882 (9) | C1—Ga1—K1 ⁱ | 76.52 (8) |
| Ga1 ⁱⁱ —K1—K1 ⁱ | 109.327 (10) | K1—Ga1—K1 ⁱ | 60.234 (17) |
| Ga1—K1—K1 ⁱ | 59.884 (9) | K1 ⁱⁱ —Ga1—K1 ⁱ | 60.233 (17) |
| F1—K1—K1 ⁱⁱ | 40.97 (2) | Ga1—C1—H1A | 109.5 |
| F1 ⁱ —K1—K1 ⁱⁱ | 84.06 (4) | Ga1—C1—H1B | 109.5 |
| F1 ⁱⁱ —K1—K1 ⁱⁱ | 40.97 (2) | Ga1—C1—H1B | 109.5 |

Symmetry codes: (i) $x, -y+1, -z+1$; (ii) $-x+1, y, -z+1$; (iii) $x, -z+3/2, -y+1$; (iv) $-z+3/2, y, -x+1$; (v) $y, x, z-1/2$; (vi) $-x+1, -y+1, z$; (vii) z, x, y ; (viii) y, z, x .

Fig. 1

