# Disodium Tetrasupersilyltetragallanediide $Na_2Ga_4R^*_4{\cdot}2THF$ ($R^* = SitBu_3$) − Preparation of a Novel Gallium Cluster Compound via Dichlorodisupersilyldigallane $R^*_2Ga_2Cl_2$[‡]

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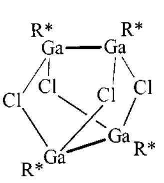
**Keywords:** Clusters / Gallium / Oligogallanes / Silicon / Sodium

Red tetragallanediide $Na_2Ga_4R^*_4{\cdot}2THF$ was prepared by reduction of the monogallane $R^*GaCl_2{\cdot}THF$ in heptane or the *tetrahedro*-tetragallane $R^*_4Ga_4$ in benzene/tetrahydrofuran (THF) with sodium at 100 °C. Potassium worked analogously as a reduction agent. As an intermediate of the dehalogenation of $R^*GaCl_2{\cdot}THF$, the orange digallane $R^*_2Ga_2Cl_2$ and the dark violet tetrahedrane $R^*_4Ga_4$ were formed. The extreme air- and moisture-sensitive $Na_2Ga_4R^*_4{\cdot}2THF$ was stable against $Me_3SiCl$, but reacted with oxygen under formation of $R^*_4Ga_4$, and with GaBr under formation of several products (isolation and X-ray structure analysis of $R^*GaBr_2{\cdot}THF$). According to X-ray structure analyses, (i) the tetragallanediide contains a nonplanar $Ga_4$ ring with short Ga–Ga bonds, whereby three Ga atoms on opposite sides of the ring are each connected with one of the two Na(THF) groups, (ii) the digallane is dimeric, whereby it takes the structure of $As_4S_4$ (exchange of As/S against Ga/Cl). The possible ways of $R^*GaCl_2{\cdot}THF$ reduction are discussed, an explanation of the structure of $Na_2Ga_4R^*_4{\cdot}2THF$ is given, and halides $R_nE_nHal_2$ (E = Al–Tl) are presented.

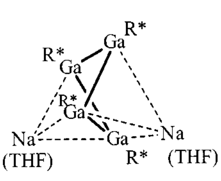
## Introduction

Uncharged or negatively charged cluster compounds $R_mE_n$ of the heavier main group III elements Al, Ga, In, Tl have − unlike such compounds with clusters of boron B[1] − only been known quite recently. In fact, the former clusters tend to disproportionate into $R_3E$ and E (or $R_2$ and E). However, this process can be hindered by employing bulky substituents R.

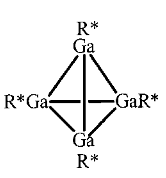
A particularly great number of sterically overloaded, non- or negatively charged clusters $R_mGa_n$ of gallium, the element that forms the focus of this publication, have been synthesized to date (cf. ref.[2] and references for over 30 gallium cluster compounds cited therein). For example, with supersilyl ($SitBu_3 = R^*$) which we use as a bulky substituent R, the following gallium cluster compounds have hitherto been prepared: $R^*_3Ga_2^{\cdot}$,[3] $R^*_3Ga_2^-$,[3] $R^*_4Ga_3^{\cdot}$,[3] $R^*_4Ga_3^-$,[3] $R^*_4Ga_4$,[4] $R^*_6Ga_8$,[5] $R^*_6Ga_8^{2-}$,[5] $R^*_6Ga_{10}^-$,[6] $R^*_6Ga_{13}^-$,[6] $R^*_8Ga_{18}$,[2] and $R^*_8Ga_{22}$.[2] Herein, we report on the reduction of $R^*GaCl_2{\cdot}THF$ with alkali metals M. This led, via the dimeric digallane $R^*_2Ga_2Cl_2$ (**1**) and the already known[4] tetrahedrane $R^*_4Ga_4$ (**3**), to the cluster compound $Na_2Ga_4R^*_4{\cdot}2THF$ (**2**). This cluster **2** contains the dianion $R^*_4Ga_4^{2-}$, which, after dark-red $Tip_6Ga_4^{2-}$ (Tip = 2,4,6-$iPr_3C_6H_2$)[7] and dark-red $Dis_2Ga_4^{2-}$ [Dis = 2,6-$(Tip)_2C_6H_3$],[8] represents a third tetragallanediide thus far prepared with a novel butterfly-shaped $Ga_4$ framework [$Tip_6Ga_4^{2-}$ contains a star-shaped $Ga_4$ framework, similar to the neutral, light orange $Tip_6Ga_4$,[7] and $Dis_2Ga_4^{2-}$ (neutral species unknown) contains a square-shaped $Ga_4$ framework[8]]. Dimeric $R^*_2Ga_2Cl_2$, on the other hand, is analogously structured as the already published dimeric $R_2E_2X_2$ with E/R = Ga/$Si(SiMe_3)_3$ [9] and In/$C(SiMe_3)_3$ [10] (X in each case is Cl or Br). Indeed, there have also been indications of the existence of $R^*_2E_2Hal_2$ with other main group III elements E ($R^*_2B_2Cl_2$, $R^*_2In_2Br_2$, $R^*_2Tl_2Br_2$ among others),[11] but to date no X-ray structure analyses exist from the latter compounds.



**1**
(orange)



**2**
(red)



**3**
(dark violet)

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[‡] Compounds of Silicon and Homologues, 151; Compounds of Boron and Homologues, 19. − Part 150 and 17: Ref.[11]

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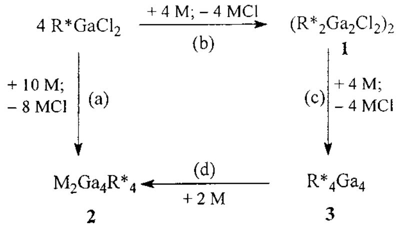
## Results and Discussion

### Syntheses and Reactions of 1 and 2

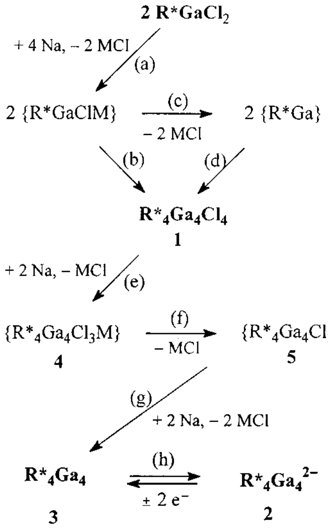
As was stated in a preceding publication,[12] the reduction of $R^*GaCl_2{\cdot}THF$ (THF = tetrahydrofuran) with sodium in heptane at 100 °C gave, according to equation (a) in Scheme 1, the violet tetrasupersilyl-*tetrahedro*-tetragallane $R^*_4Ga_4$ (**3**) and an unidentified water- and oxygen-sensitive red gallium cluster compound. We have since been able to identify the red compound as $Na_2Ga_4R^*_4{\cdot}2THF$ (**2**) (see Scheme 1; interestingly, the reaction of homologous $R^*AlCl_2{\cdot}THF$ with Na does not proceed in this way; see ref.[12]). As with sodium, potassium reduced $R^*GaCl_2{\cdot}THF$ under formation of a THF adduct of $K_2Ga_4R^*_4$. After filtration of the insoluble material and exchange of heptane for benzene, the tetragallanediide slowly crystallized (in weeks) at 5 °C as red prisms that were extremely water- and oxygen-sensitive. Indeed, in the presence of traces of air the tetragallanediide was oxidized to **3** according to $R^*_4Ga_2^{2-} \leftrightarrows R^*_4Ga_4 + 2e^-$ [reverse of equation (d) in Scheme 1]. Thereby, the tetrahedrane was formed as an intermediate that itself rapidly reacted with oxygen under formation of the heterocubane $R^*_4Ga_4O_4$ [the latter hydrolyzed to $R^*Ga(OH)_2$].[4] Certainly, oxidation of **2** with R*Br should quantitatively lead to **3** (ref.[3]).



Scheme 1. Reaction of $R^*GaCl_2{\cdot}THF$ with alkali metals M = Na, K (THF excluded for clarity; R* = Si*t*Bu₃)

Besides **3**, as a further intermediate of the reduction of $R^*GaCl_2{\cdot}THF$ with alkali metals, the water- and oxygen-sensitive digallane $(R^*_2Ga_2Cl_2)_2$ (**1**) could be isolated as orange crystals [equation (b) in Scheme 1]. The reduction of **1** then led, by way of the tetrahedrane **3**, to the tetragallanediide **2** [equation (c) and (d) in Scheme 1]. In fact, **3** could be reduced according to equation (d) in Scheme 1 with Na in a mixture of benzene and THF at 100 °C. In this respect, the latter reaction offered another possibility for producing **2**.

Certainly, the first reaction of $R^*GaCl_2{\cdot}THF$ with M = Na or K – leading via **1** and **3** to **2** – consists of an exchange of chlorine by M [equation (a) in Scheme 2]. Possibly, R*GaClM forms from $R^*GaCl_2{\cdot}THF$/Na via the radical $R^*GaCl^{\cdot}$, which would then be rapidly reduced by Na. Therefore, the radical concentration would remain low, forestalling a radical dimerization. In fact, the formed gallanide R*GaClM could obviously then react with the starting material $R^*GaCl_2$ under formation of **1** [equation (b) in Scheme 2] or might – more probably for steric reasons – eliminate MCl with formation of the gallylene R*Ga, which after insertion into a Ga–Cl bond of $R^*GaCl_2$ would give the isolated product **1** [equations (c), (d) in Scheme 2; cf. dehalogenation of $R^*SiHal_3$ (ref.[13])].



Scheme 2. Possible ways from $R^*GaCl_2{\cdot}THF$/Na in heptane at 100 °C, via **1** (and perhaps **4** and **5**) to **3** and its reduction product **2** (M = Na or K; R* = Si*t*Bu₃; THF excluded for clarity); bold-face formulae refer to isolated products

Further intermediates on the way from $R^*GaCl_2{\cdot}THF$ to **3** were definitively not seen. Obviously, all these formed much more slowly from reactants than they transformed into following products. Certainly, many ways are imaginable that lead to the tetragallanediide. To our mind, the reaction of **1** with M transforms via $R^*_4Ga_4Cl_3M$ (**4**) and $R^*_4Ga_4Cl_2$ (**5**) into **3** [equations (e), (f), and (g) in Scheme 2]. A fast reduction of **3** finally gives **2** [equation (h) in Scheme 2]. In fact, compounds related to **4** and **5**, namely $R_4Ga_4I_3^-$ [R = $Si(SiMe_3)_3$][6] and $R_4In_4Br_2$ [R = $C(SiMe_3)_3$][10] could be isolated (cf. Figure 4; compound **5** might be prepared by mild chlorination of **3**).

### Structures of 1, 2, and $R^*GaBr_2{\cdot}THF$

Figure 1 shows the structure of the molecule $Na_2Ga_4R^*_4{\cdot}2THF$ (**2**) in the crystal (red prisms, monoclinic, *C*2/*c*) together with selected bond lengths and angles. The central structural element of **2** is a nonplanar, butterfly-shaped $Ga_4$ ring with nearly equal Ga–Ga bond lengths (2.43 Å; distances of opposite Ga atoms 3.21 Å), and nearly equal Ga–Ga–Ga bond angles (82.6°) as well as Ga–Ga–Ga–Ga torsion angles (39.4°; the angle between the Ga–Ga–Ga planes amounts to 122.9°). In the course of the two-electron reduction of the tetrahedrane $R^*_4Ga_4$ (Ga–Ga distances 2.57 Å[4]) the Ga–Ga bonds shorten (by 0.14 Å on average) and the $Ga_4$ cluster opens. In fact, the Ga–Ga distances in **2** are comparable to the Ga–Ga bond length in $R^*_2Ga\dot{-}GaR^*$ (2.43 Å), which itself relates to a bond order of 1.5 (see ref.[3]; the mean Ga–Ga distances in

$Tip_6Ga_4$,[7] $Tip_6Ga_4^{2-}$,[7] and $Dis_2Ga_4^{2-}$ [8] amount to 2.47, 2.39 and 2.46 Å).

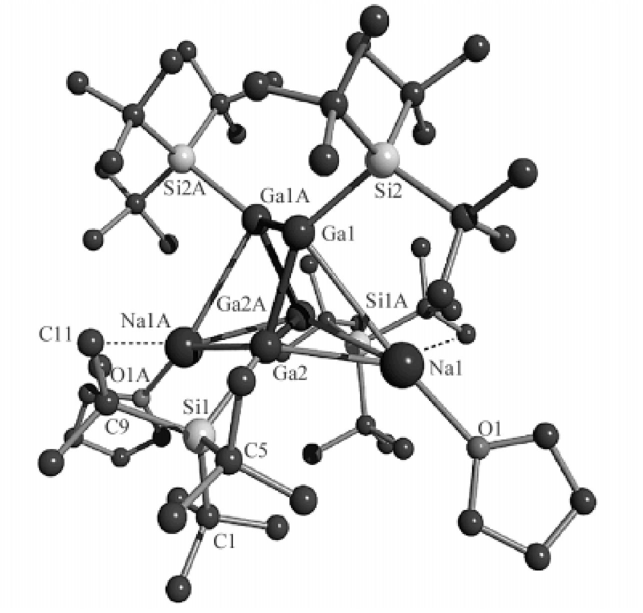


Figure 1. A view of molecule **2** (local symmetry $C_2$) in the crystal (H atoms excluded for clarity); the dotted line represents the (electrostatic) contacts of $Na^+$ with a $CH_3$ group of Si*t*$Bu_3$; selected bond lengths [Å] and angles [°]: Ga1−Ga1A 2.416(1), Ga1−Ga2 2.4238(6), Ga1−Si2 2.4488(9), Ga1−Na1 3.470(1), Ga1−Ga2A 3.206(1) Ga2−Si1 2.4401(8), Ga2−Ga2A 2.4530(8), Ga2−Na1 2.934(1), Ga2−Na1A 3.303, Si−C (mean value) 1.96, C11−Na1A 2.988(4), Na1−O1 2.252(3); Ga1A−Ga1−Ga2 82.98(1), Ga1A−Ga1−Si2 132.11(3), Ga2−Ga1−Si2 140.49(2), Ga1A−Ga1−Na1 106.74(3), Ga2−Ga1−Na1 56.41(3), Si2−Ga1−Na1 91.32(3), Ga1−Ga2−Si1 133.30(2), Ga1−Ga2−Ga2A 82.20(2), Si1−Ga2−Ga2A 142.99(2), Ga1−Ga2−Na1 80.11(3), Si1−Ga2−Na1 115.52(4), Ga2A−Ga2−Na1 75.03(4), Ga1−Ga2−Na1A 111.70(3), Si1−Ga2−Na1A 92.33(4), Ga2A−Ga2−Na1A 59.12(4), Na1−Ga2−Na1A 129.14(3), C−Si−C (mean value) 110.1; Ga1−Ga2−Ga2A−Ga1A 39.32, Ga2−Ga2A−Ga1A−Ga1 39.39

To explain the structure of **2**, one can assume that each Na atom transfers its s electron *entirely* to the $Ga_4$ cluster, which then works as a 2π-aromatic system with shortened and nearly equal Ga−Ga bonds (see Figure 2a). Obviously, the nonplanarity of the $Ga_4$ ring in **2** is, in this case, a consequence of steric hindrance of the four supersilyl groups with respect to each other (as a consequence of the overcrowding, **2** does not react with $Me_3SiCl$). Incidentally, 1,2-dihydro-1,3-diborets $R_4B_2C_2$ (R = organyl, silyl) also show a nonplanar 2π-aromatic $B_2C_2$ ring.[14]

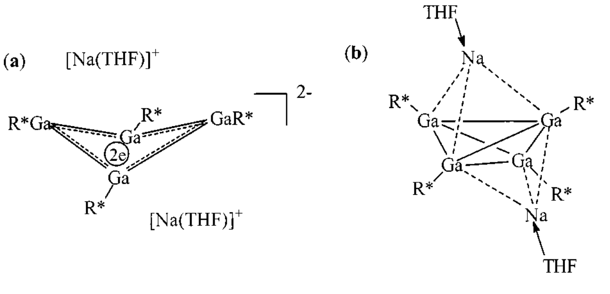


Figure 2. Illustration of the central framework of **2** (a) as a 2π-aromatic system, (b) as a twofold-capped tetrahedron

If on the other hand, each Na atom transfers its s electron only *partly* to $Ga_4$ in **2**, the $Na_2Ga_4$ framework of the molecule must be viewed as a whole. The Wade-Mingos rules (cf. ref.[1]) − which associate the number of cluster electrons with the cluster structure − predict a bicapped tetrahedron (see Figure 2b) for the $Na_2Ga_4$ part of **2**, according to the present $10 = 2n - 2$ cluster electrons [$n$ = number of cluster atoms that deliver 1 electron (Na·THF) or 2 electrons (GaR*) each]. An argument for the latter description is the stability of the tetragallanediide even in pure THF [no indication of formation of independent cations $Na(THF)_n^+$]. Therefore, it might be imaginable that the reaction of **2** with GaBr results in an exchange of $Na(THF)^+$ against the "isoelectronic" $Ga^+$ under production of the novel gallium cluster compound $R^*_4Ga_6$ which is in great demand. In fact, **2** and GaBr transform in pentane/toluene/THF into the gallane $R^*GaBr_2$·THF (see below) and other products (not identified to date).

According to Figure 1, the Na atoms in **2** are each coordinated with three Ga atoms (Na−Ga distances 2.93/3.30/3.45 Å) on opposite sides of the $Ga_4$ ring, and in addition with the O atom of one THF molecule (Na−O distance 2.52 Å), as well as one $CH_3$ group of the substituents Si*t*$Bu_3$ (Na−C distance 2.99 Å). The mean values of the Si−Ga bond lengths (2.44 Å), C−Si bond lengths (1.96 Å), and C−Si−C bond angles (110.1°) are normal for supersilylated gallium cluster compounds.[2−6]

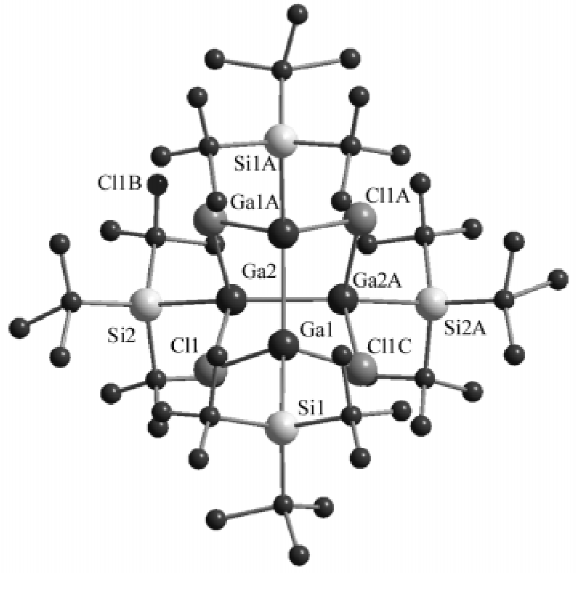
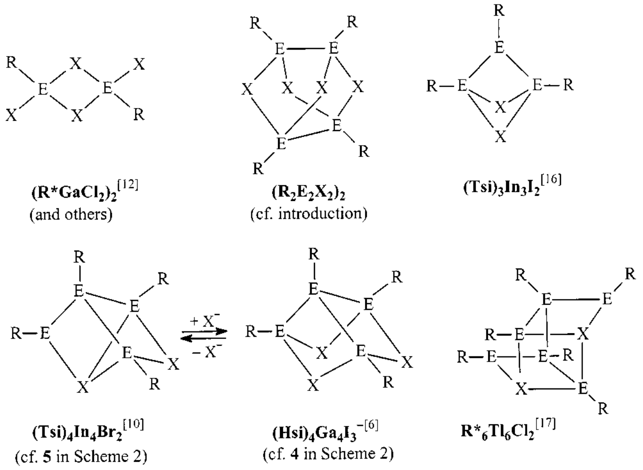


Figure 3. A view of the molecule **1** (local symmetry approx. $S_4$) in the crystal (H atoms excluded for clarity); selected bond lengths [Å] and angles [°]: Ga1−Ga1A/Ga2−Ga2A 2.546(3)/2.548(3), Ga1−Cl1/Ga2−Cl1 2.415(3)/2.403(3), Ga1−Si1/Ga2−Si2 2.473(4)/2.469(4), Si−C (mean value) 1.95; Cl1−Ga1−Cl1C/Cl1−Ga2−Cl1B 90.6(2)/90.6(2), Cl1−Ga1−Ga1A/Cl1−Ga2−Ga2A 100.38(9)/100.58(9), Ga1−Cl1−Ga2 101.72(10), Cl1−Ga1−Si1/Cl1−Ga2−Si2 104.96(9)/104.46(9), Si1−Ga1−Ga1A/Si2−Ga2−Ga2A 143.64(9)/144.07(9), C−Si−C (mean value) 112.0, C−Si−Ga (mean value) 106.8

Figure 3 shows the structure of the molecule $R^*_4Ga_4Cl_4$ (**1**) together with selected bond lengths and angles. Hereafter, dichlorodisupersilyldigallane $R^*_2Ga_2Cl_2$ represents a dimer, whereby the central $Ga_4Cl_4$ framework is structured analogously to $As_4S_4$ [1] [exchange of As/S by Ga/Cl; $(HGa)_4Cl_4$ is isoelectronic with $As_4S_4$]. The Ga atoms are distorted-tetrahedrally coordinated by Si, Ga, and 2Cl (angles Si−Ga−Cl/Si−Ga−Ga/Cl−Ga−Ga/Cl−Ga−Cl ca. 105/144/100/90°). The Cl atoms are two-coordinated by 2Ga (angle Ga−Cl−Ga ca. 102°). The two $R^*Cl_2Ga-GaCl_2R^*$ moieties show eclipsed conformations.



**$(R^*GaCl_2)_2$**[12]
(and others)

**$(R_2E_2X_2)_2$**
(cf. introduction)

**$(Tsi)_3In_3I_2$**[16]

**$(Tsi)_4In_4Br_2$**[10]
(cf. **5** in Scheme 2)

**$(Hsi)_4Ga_4I_3^-$**[6]
(cf. **4** in Scheme 2)

**$R^*_6Tl_6Cl_2$**[17]

Figure 4. Examples of dihalides with the formulae $R_nE_nX_2$ [R = Si*t*Bu$_3$ (R*), $Si(SiMe_3)_3$ (Hsi), $C(SiMe_3)_3$ (Tsi); E = Al−Tl; X = halogen] and their adducts with halides [e.g. $REX_3^-$,[8] $R_2E_2X_4^{2-}$,[8] and $R_4E_4X_3^-$ (see above)[8]]; for monohalides $R_{n-1}E_nX$ with $n$ = 1, 2, 3 see refs.[11,12,17]

The Ga−Ga distances in **1** (2.55 Å) are longer than those in the hitherto studied digallanes $R_4Ga_2$, $R_2Ga_2Hal_2$ (monomer or dimer), $R_2Ga_2Hal_4^{2-}$, $R_2Ga_2Hal_2{\cdot}2D$ (D = ethers, amines, phosphanes), and $Ga_2Hal_6^{2-}$ (2.39 to 2.54 Å).[3] Thereby, the Ga−Ga bond lengths shorten by going from $R^*_4Ga_4Cl_4$ [2.55 Å; R* = supersilyl $Si(CMe_3)_3$] to the analogously structured $R_4Ga_4Cl_4$ [2.50 Å; R = hypersilyl $Si(SiMe_3)_3$][9] due to steric effects. Certainly, the size of the supersilyl groups is not sufficient to prevent a dimerization of $R^*_2Ga_2Cl_2$, as is true for $Mes^*_2Ga_2Cl_2$ (Mes* = supermesityl = 2,4,6-*t*Bu$_3$C$_6$H$_2$),[15] but obviously it hinders the transformation of **1** into an adduct $R^*_2Ga_2Cl_2{\cdot}2THF$ in the presence of THF. The Ga−Cl distances in **1** (2.42 Å) are significantly longer than those in dimeric $R^*GaCl_2$ (2.18 to 2.39 Å) or monomeric $R^*_2GaCl$ (2.25 Å).[12]

Indeed, dimeric **1** represents one member of compounds of formulae $R^*_nGa_2Cl_{4-n}$ or more generally, $R_nGa_2Hal_{4-n}$ with $n = 2$. Among the other members, $R^*_3Ga_2Cl$ ($n = 3$) is possibly obtained as the product of chlorination of the radical $R^*_3Ga_2^{\cdot}$,[3] whereas $R^*_4Ga_2$ ($n = 4$) loses R* and exists only as radical $R^*_3Ga_2^{\cdot}$.[11] The digallanes $R^*Ga_2Cl_3$ ($n = 1$) and $Ga_2Cl_4$ ($n = 0$) are unknown to date. Certainly, $Ga_2Cl_4$, with a structure like **1** (exchange of R* with Cl, e.g. by reaction of **1** with HCl in alkanes at low temperatures) is isomeric to the long-known $Ga^+GaCl_4^-$.[1]

On the other hand, $R^*_2Ga_2Cl_2$ represents one homologue of compounds of formulae $R^*_nGa_nCl_2$, or more generally, $R_nE_nHal_2$ (E = triel = element of the third main group), that are themselves halogen derivatives, $R^*_{n+2-m}E_nHal_m$, of compounds with the general formulae $R^*_{n+2}E_n$ ($m = 0$). Figure 4 shows some examples of $R_nE_nHal_2$ and their ad-

Table 1. Selected parameters from the X-ray structure analyses of $Na_2Ga_4R^*_4{\cdot}2THF$ (**2**), $(R^*_2Ga_2Cl_2)_2$ (**1**), and $R^*GaBr_2{\cdot}THF$

| | $Na_2Ga_4R^*_4{\cdot}2THF$ (**2**) | $(R^*_2Ga_2Cl_2)_2$ (**1**) | $R^*GaBr_2{\cdot}THF$ |
|---|---|---|---|
| Empirical formula | $C_{56}H_{124}Ga_4Na_2O_2Si_4$ | $C_{48}H_{108}Cl_4Ga_4Si_4$ | $C_{16}H_{35}Br_2OSi$ |
| $M_r$ | 1266.84 | 1218.43 | 501.07 |
| Crystal size [mm] | 0.1 × 0.2 × 0.2 | 0.25 × 0.2 × 0.2 | 0.3 × 0.5 × 0.5 |
| System | monoclinic | orthorhombic | orthorhombic |
| Space group | *C2/c* | *Cmcm* | *Pbca* |
| $a$ [Å] | 24.274(5) | 23.855(7) | 13.784(3) |
| $b$ [Å] | 12.863(3) | 13.654(3) | 13.301(3) |
| $c$ [Å] | 24.683(5) | 23.814(5) | 24.049(5) |
| β [°] | 116.62(3) | 90.00 | 90.00 |
| $V$ [Å$^3$] | 6890(3) | 7757(3) | 4409(2) |
| $Z$ | 4 | 4 | 8 |
| D [mg m$^{-3}$] | 1.217 | 1.074 | 1.510 |
| $F$(000) | 2696 | 2660 | 2032 |
| μ [mm$^{-1}$] | 1.664 | 1.599 | 4.926 |
| 2θ [°] | 4.48−52.00 | 8.58−52.04 | 4.58−51.88 |
| Refl. collected | 15373 | 20584 | 28425 |
| indep. ($R_{int}$) | 6453 (0.0312) | 3938 (0.0936) | 4289 (0.0000) |
| obsd. [$F$>4σ($F$)] | 4957 | 2489 | 2347 |
| GOOF | 0.917 | 1.075 | 0.745 |
| *h,k,l* ranges | $-29 \le h \le 26$ | $-29 \le h \le 29$ | $0 \le h \le 16$ |
| | $0 \le k \le 15$ | $-16 \le k \le 16$ | $0 \le k \le 16$ |
| | $0 \le l \le 30$ | $-29 \le l \le 29$ | $-29 \le l \le 0$ |
| $R1$ [$F$>4σ($F$)] | 0.0326 | 0.0994 | 0.0393 |
| $wR2$ (all data) | 0.0778 | 0.2777 | 0.0931 |
| max./min. diff peak [e·Å$^{-3}$] | 0.524/−0.429 | 1.306/−0.824 | 1.020/−0.869 |

ducts with halogenides, the structures of which are known (obviously, the Ga atoms in $R_nE_nHal_2$ try to obtain the coordination number 4 by forming inter- or intramolecular halogen bridges).

The molecule $R^*GaBr_2 \cdot THF$, which was obtained as one of the products of the reaction of **2** with GaBr (see above), but has already been synthesized by reaction of $GaBr_3$ with NaR* in THF[12] is analogously structured as the other donor adducts $R^*EHal_2 \cdot D$ (E = B to Tl),[12] and shows a distorted tetrahedral coordination of Ga with one Si atom (from R*), two Cl atoms, and one O atom (from THF). For bond lengths and angles of dibromosupersilylgallane−tetrahydrofuran(1:1), the structure of which is not discussed in detail, see ref.[18]. Further data can be found in Table 1.

## Experimental Section

**General:** All experiments were performed under purified nitrogen or in vacuo, using Schlenk techniques. Available for use were: Na, K, $C_6D_6$, $C_4D_8O$, $Me_3SiCl$, and the solvents heptane, benzene, and tetrahydrofuran. The following compounds were synthesized according to literature procedures: $R^*GaCl_2 \cdot THF$,[12] and $R^*_4Ga_4$ (**3**).[4] For NMR spectra a Jeol GSX-270 and Jeol EX-400 were available. The $^{29}Si$ NMR spectra were recorded with the INEPT or DEPT pulse sequence using empirically optimized parameters for the mentioned groups.

**Synthesis of the THF Adducts of $M_2Ga_4R^*_4$ (M = Na, K). − (i):** 0.402 g (0.975 mmol) of $R^*GaCl_2 \cdot THF$ and 1.00 g (43.5 mmol) of Na were heated for 7 h in 20 mL of heptane at 100 °C. According to NMR ($C_6D_6$), the reaction mixture (now red) then contained compound **2**. After filtration of the heptane-insoluble materials, evaporation of volatile products under an oil-pump vacuum, and dissolution of the residue in 5 mL of benzene, 0.080 g (0.06 mmol; 26%) of disodium tetrasupersilyltetragallanediide−tetrahydrofuran(1:2) (**2**) was obtained in 8 weeks at 5 °C as water- and oxygen-sensitive, red prisms. $^1H$ NMR ($C_6D_6$, int. TMS): $\delta$ = 1.47 (broad, 4 Si, Si*t*Bu$_3$), 1.32/3.40 (m/m, 8 H/8 H, $CH_2/CH_2O$). $^{13}C\{^1H\}$ NMR ($C_6D_6$, int. TMS): $\delta$ = 23.1/25.2 (s/s, 6 C/6 C, *C*Me$_3$/*C*Me$_3$), 30.2/34.4 (s/s, 18 C/18 C, C*Me$_3$*/C*Me$_3$*), 25.5/67.9 (s/s, 8 H/8 H, $CH_2/CH_2O$). $^{29}Si\{^1H\}$ NMR ($C_6D_6$, ext. TMS): $\delta$ = 40.7/48.6 (s/s, 2 Si/2 Si, Si*t*Bu$_3$/Si*t*Bu$_3$). X-ray structure analysis: see Figure 1. Remarks: a) The insoluble material of the reaction mixture consists of **3**, among others; identification by comparison with an authentic sample[4]. It was separable from insoluble Na and NaCl by dissolving it in 10 mL of THF (see ref.[12]). b) After dissolving 0.015 g (0.01 mmol) of **2** in 0.5 mL of [D$_8$]THF, no changes in color or NMR spectra were observed. − **(ii):** Heating of **3** (0.095 g, 0.88 mmol) and 0.005 g (0.218 mmol) of Na in 0.4 mL of $C_6D_6$/0.1 mL of THF for 2 h at 100 °C led − according to NMR − exclusively to the formation of **2**. For characterization see above. − **(iii):** The reaction of $R^*GaCl_2 \cdot THF$ with K in heptane at 100 °C (cf. reaction with Na, above) led to a solution, in 7 h, containing a substance that was probably a THF adduct of dipotassium tetrasupersilyltetragallanediide $K_2Ga_4R^*_4$. The $^1H$, $^{13}C$, and $^{29}Si$ NMR shifts of this substance were identical with those for **2** (see above).

**Reactions of the THF Adducts of $M_2Ga_4R^*_4$ (M = Na, K). − (i):** Red **2** (0.015 g, 0.01 mmol) in 0.5 mL of $C_6D_6$ reacted with traces of oxygen, in the first instance under formation of the violet tetrahedrane **3**, which then transformed into the colorless heterocubane $R^*_4Ga_4O_4$ (identification of the products by comparison with authentic samples[4]). Obviously, the same is valid for the THF adduct of $K_2Ga_4R^*_4$. − **(ii):** Chlorotrimethylsilane ($Me_3SiCl$) did not react with **2** in benzene even at 100 °C. − **(iii):** Gallium monobromide (GaBr)[19] (0.9 mmol) in 3 mL of toluene/1 mL of THF was added to 0.4 mmol of **2** in 20 mL of heptane at −78 °C. After warming the solution to room temperature, and evaporation of volatile products under an oil-pump vacuum, a dark brown residue was obtained. Extraction of the latter with pentane gave a metallic residue (Ga) and a violet solution that contained several compounds, according to NMR. Colorless crystals of dibromosupersilylgallane−tetrahydrofuran(1:1) $R^*GaBr_2 \cdot THF$ (identified by comparison with an authentic sample[12] and by X-ray structure analysis) were obtained from the pentane extract. Obviously, the solution contains in addition, violet tetrasupersilyl-*tetrahedro*-tetragallane (**3**) among others.

**Synthesis of Dimeric $R^*_2Ga_2Cl_2$ (1):** $R^*GaCl_2 \cdot THF$ (0.514 g, 1.247 mmol) and 1.50 g (38.4 mmol) of K were heated for 2 h in 40 mL of heptane at 100 °C. According to NMR, the solution then contained **1** (besides small amounts of $R^*GaCl_2 \cdot THF$ and the THF adduct of $K_2Ga_4R^*_4$). After filtration of the insoluble materials (K and KCl), evaporation of the volatile products under an oil-pump vacuum, and dissolution of the residue in 8 mL of heptane, 0.09 g (0.07 mol; 28%) of the dimeric dichlorotetrasupersilyldigallane $R^*_2Ga_2Cl_2$ (**1**) was obtained in 6 weeks at −25 °C as water- and oxygen-sensitive orange crystals. $^1H$ NMR ($C_6D_6$, int. TMS): $\delta$ = 1.346 (s, 108 H, Si*t*Bu$_3$). $^{13}C\{^1H\}$ NMR ($C_6D_6$, int. TMS): $\delta$ = 25.2/32.6 (s/s, 12 C/36 C, *C*Me$_3$/C*Me$_3$*). $^{29}Si\{^1H\}$ NMR ($C_6D_6$, ext. TMS): $\delta$ = 30.9 (s, 4 Si, Si*t*Bu$_3$). X-ray structure analysis: see Figure 3. Remarks: The $^{29}Si$ NMR signal at $\delta$ = 30.9 was also observed, besides signals for $R^*GaCl_2 \cdot THF$ and for **2** by way of the reaction of $R^*GaCl_2 \cdot THF$ with Na in heptane at 100 °C after 30 min. Consequently, **1** was also intermediately formed during the reduction of $R^*_2GaCl \cdot THF$ with Na.

**X-ray Structure Determinations:** Data collections were performed using Mo-$K_\alpha$ radiation with a STOE IPDS diffractometer at $T$ = 200 K (**2**, $R^*GaBr_2 \cdot THF$) or with a Siemens SMART diffractometer at 193 K (**1**). Structures were solved with direct methods. Refinement was with full matrix on $F^2$. All non-hydrogen atoms were included as riding models with fixed isotropic $U$ values in the final refinement. Due to high thermal motion and disordering within the Si*t*Bu$_3$ substituents only a rather poor-quality X-ray structure determination of **1** was achieved. For further data, see Table 1. Crystallographic data (excluding structure factors) for the structures reported have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-165315 (**2**), -167434 (**1**), and -167745 ($R^*GaBr_2 \cdot THF$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

## Acknowledgments

We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support.

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[1] See textbooks of Inorganic Chemistry.

[2] A. Donchev, A. Schnepf, G. Stößer, E. Baum, H. Schnöckel, T. Blank, N. Wiberg, *Chem. Eur. J.* **2001**, 3348−3353.

[3] N. Wiberg, T. Blank, K. Amelunxen, H. Nöth, J. Knizek, T. Habereder, W. Kaim, M. Wanner, *Eur. J. Inorg. Chem.* **2001**, 1719−1727.

[4] N. Wiberg, K. Amelunxen, H.-W. Lerner, H. Nöth, W. Ponikwar, H. Schwenk, *J. Organomet. Chem.* **1999**, *574*, 246−251.

[5] N. Wiberg, T. Blank, H. Nöth, M. Suter, M. Warchhold, *Eur. J. Inorg. Chem.*, in press.

[6] M. Kehrwald, W. Köstler, A. Rodig, G. Linti, T. Blank, N. Wiberg, *Organometallics* **2001**, *20*, 860−867.

[7] R. J. Wehmschulte, P. P. Power, *Angew. Chem.* **1998**, *110*, 3344−3346; *Angew. Chem. Int. Ed.* **1998**, *37*, 3152−3154.

[8] B. Twamley, P. P. Power, *Angew. Chem.* **2000**, *112*, 3643−3646; *Angew. Chem. Int. Ed.* **2000**, *39*, 3500−3503.

[9] A. Schnepf, E. Weckert, G. Linti, H. Schnöckel, *Angew. Chem.* **1999**, *111*, 3578−3581; *Angew. Chem. Int. Ed.* **1999**, *38*, 3381−3383; G. Linti, W. Köstler, *Angew. Chem.* **1996**, *108*, 593−595; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 550−552.

[10] W. Uhl, S. Melle, *Chem. Eur. J.* **2001**, *7*, 4216−4221.

[11] N. Wiberg, T. Blank, K. Amelunxen, H. Nöth, H. Schnöckel, E. Baum, A. Purath, D. Fenske, *Eur. J. Inorg. Chem.* **2001**, 341−350.

[12] N. Wiberg, K. Amelunxen, H.-W. Lerner, H. Nöth, J. Knizek, I. Krossing, *Z. Naturforsch., Teil B* **1998**, *53*, 333−348; N. Wiberg, K. Amelunxen, T. Blank, H.-W. Lerner, K. Polborn, H. Nöth, R. Littger, M. Rackl, M. Schmidt-Amelunxen, H. Schwenk-Kircher, M. Warchhold, *Z. Naturforsch., Teil B*, **2001**, *56*, 634−651.

[13] N. Wiberg, W. Niedermayer, *J. Organomet. Chem.* **2001**, *628*, 57−64.

[14] M. Hildenbrand, H. Pritzkow, W. Siebert, *Angew. Chem.* **1985**, *97*, 769−770; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 759−760.

[15] A. H. Cowley, A. Decken, C. A. Olazabal, *J. Organomet. Chem.* **1996**, *524*, 271−273.

[16] W. Uhl, S. Melle, G. Geiseler, K. Harms, *Organometallics* **2001**, *20*, 3355−3357.

[17] N. Wiberg, T. Blank, H.-W. Lerner, D. Fenske, G. Linti, *Angew. Chem.* **2001**, *113*, 1275−1278; *Angew. Chem. Int. Ed.* **2001**, *40*, 1232−1235.

[18] Bond lengths [Å] and angles [°] of R*$GaBr_2$·THF: Ga−O 2.027(3), Ga−Br 2.360(1), Ga−Si 2.426(1), Si−C (mean value) 1.93; O−Ga−Br 98.10(10)/98.32(9), Br−Ga−Br 105.55(3), O−Ga−Si 114.32(9), Br−Ga−Si 118.88(4)/118.08(4), C−Si−C (mean value) 112.1.

[19] C. Dohmeier, D. Loos, H. Schnöckel, *Angew. Chem.* **1996**, *108*, 141−161; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 129−149.

Received August 8, 2001
[I01302]