Gallium−Gallium Bonds as Key Building Blocks for the Formation of Large Organometallic Macrocycles, on the Way to a Mesoporous Molecule

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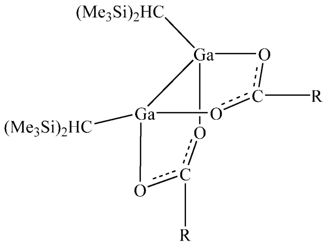
A macrocyclic gallium carboxylate (**3**) is formed on reaction of the digallane(4) $R_2Ga-GaR_2$ [$R = CH(SiMe_3)_2$], **1**, with naphthalene-2,6-dicarboxylic acid, $HOOC-C_{10}H_6-COOH$. The macrocycle comprises 44 atoms, and four Ga−Ga single bonds are connected by four dicarboxylato bridges. The cavity of the heterocycle may be described as a rigid molecular square possessing a largest diameter of 1.86 nm. It encloses four 1,2-difluorobenzene molecules.

Introduction

While the Al−Al and In−In single bonds of the organoelement compounds R_2E-ER_2 [$R = CH(SiMe_3)_2$][1,2] are readily cleaved upon treatment with carboxylic acids,[3] the Ga−Ga bond of the corresponding digallium compound **1**[4] remains intact under similar conditions. Two bis(trimethylsilyl)methyl groups are replaced by chelating carboxylato groups, which interestingly bridge the Ga−Ga bond and are arranged perpendicular to one another (**2**, Scheme 1).[5−7] Structural motifs result that often have been observed for transition metal compounds. The substituent exchange reactions proceed almost quantitatively. Owing to the particular arrangement of the bridging ligands, the formation of macrocyclic compounds is favored when bifunctional dicarboxylic acids are employed. Those acids that have a more flexible backbone give dimers with two Ga−Ga bonds bridged by the dicarboxylates,[7] while rigid backbones yield compounds containing four Ga−Ga bonds.[8] These macrocycles usually encapsulate solvent molecules, and they may be able to act as specific hosts for a broad variety of guests after some derivatization. Polymerization as a possible side reaction has not been observed so far. However, these macrocycles may be expected to become more and more unstable with increasing size. Furthermore, the growth of single crystals required for a thorough characterization of those very large heterocycles proved to be extraordinarily difficult. We report here on the largest heterocycle isolated so far in that particular gallium system.

Scheme 1



2 [$R = CH_3, C_6H_5, CMe_3$, etc.]

Results and Discussion

Tetraalkyldigallane(4) **1** reacted with naphthalene-2,6-dicarboxylic acid in THF solution at room temperature to yield the pale yellow product **3** (eq 1) in 77% yield after recrystallization from cyclopentane. Similar to the carboxylato compounds isolated before,[5−8] the resonances of the CH protons and the carbon atoms attached to gallium show a strong shift to higher field compared to the starting compound **1** (**1**: $\delta = 1.11$ and 25.9, respectively; **3**: $\delta = -0.01$ and 5.1), which is indicative for an enhancement of the coordination number of the Ga atoms from three to four. The integration ratio verifies the replacement of two bis(trimethylsilyl)methyl groups by two carboxylato ligands per each formula unit of **1**. The constitution of **3** as an octanuclear macrocycle was clarified by crystal structure determination (see below) and is schematically shown in eq 1. Compound **3** is rather stable in the solid state and does not decompose until 380 °C; however, a slight darkening of the solid was determined above 300 °C. In contrast, slow decomposition occurred in solution at room temperature and day light, which resulted in the formation of a colorless solid insoluble in organic solvents. The IR spectrum of that solid is almost indistinguishable from that of the pure product **3**, and we suppose that a polymer was formed by ring-opening.

All attempts to generate single crystals from different solvents such as cyclopentane, toluene, or THF failed

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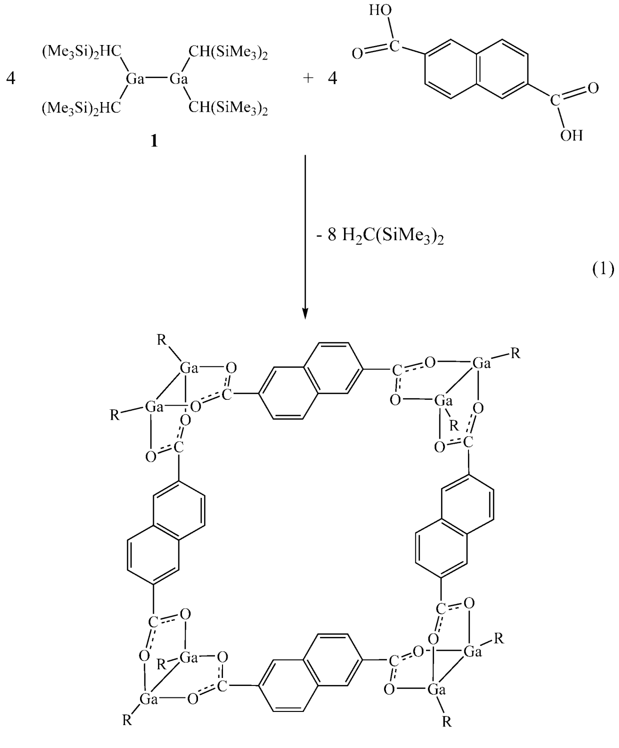


3 [R = $CH(SiMe_3)_2$]

and yielded amorphous or poorly crystalline solids only. Finally, we obtained crystals suitable for a structure determination from 1,2-difluorobenzene. The molecular structure of compound **3** (Figure 1) contains four Ga−Ga single bonds bridged by four dicarboxylato ligands and comprises a large macrocycle formed by 44 atoms. Thus, the Ga−Ga bond once again shows its excellent capability to favor molecular self-assembly with the high yield formation of large macrocycles. Owing to the rigidity of the bridging ligands, an almost squaric cavity is formed which has an impressively large diameter of 1.84−1.86 nm [Ga(1)−Ga(2′) and Ga(3)−Ga(4′), respectively]. The Ga−Ga separations along the edges of the cavity [Ga(1)−Ga(3), Ga(1)−Ga(4′), Ga(2)−Ga(3′), Ga(2)−Ga(4)] are in a very narrow range around 1.31 nm. Transannular distances between the inner carbon atoms of the naphthalene groups differ by 160 pm [C(015)···C(01b) and C(016)···C(01a) 1.41 nm; C(035)···C(03b) and C(036)···C(03a) 1.25 nm)] and indicate a curvature of the spacers and a slight deviation from the ideal squaric form. The Ga−Ga bond lengths (239.2 pm), the perpendicular arrangement of the carboxylato groups (angles O−Ga−O 92.5° on average), and other structural parameters are quite similar to those observed before for other carboxylato-bridged digallium compounds[5−8] and do not need further discussion. The naphthyl bridges are almost ideally in plane with the carboxylato groups. The angles between the normals of the average planes show small values between 5.1° and 7.4°. Compound **3** crystallizes with eight 1,2-difluorobenzene molecules per each formula unit. Four solvent molecules are almost ideally in the plane of the heterocycle and are encapsulated by the large macrocycle. They are arranged perpendicular to one another so that each one is parallel and near to one bridging ligand. The remaining four solvent molecules are located between the bulky substituents above and below opposite sides of the heterocycle.

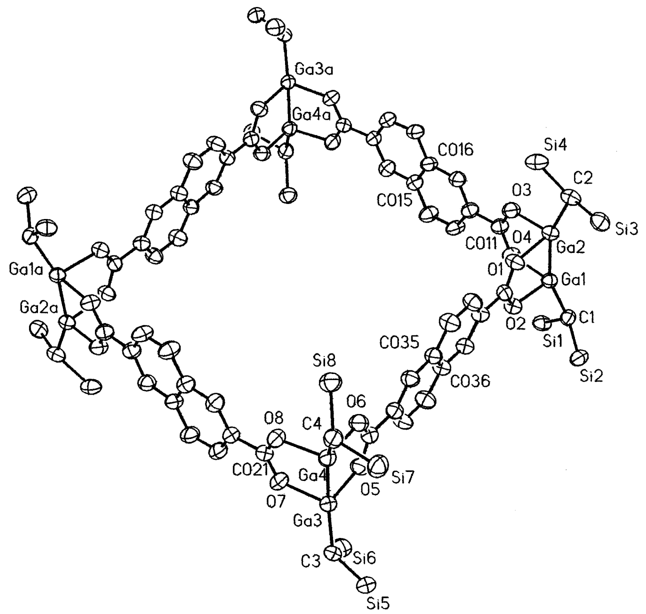
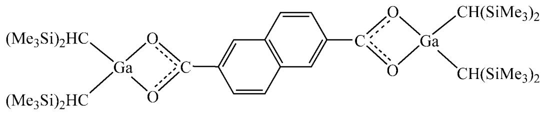


Figure 1. Molecular structure of **3**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups and hydrogen atoms are omitted for clarity. Important bond lengths (Å) and angles (deg): Ga(1)−Ga(2) 239.60(9), Ga(3)−Ga(4) 238.8(1), Ga(1)−O(1) 201.2(4), Ga(1)−O(2) 202.4(4), Ga(2)−O(3) 200.6(4), Ga(2)−O(4) 201.7(4), Ga(3)−O(5) 201.1(5), Ga(3)−O(7) 200.3(4), Ga(4)−O(6) 201.3(5), Ga(4)−O(8) 202.4(4), O(1)−Ga(1)−O(2) 90.3(2), O(3)−Ga(2)−O(4) 93.1(2), O(5)−Ga(3)−O(7) 93.5(2), O(6)−Ga(4)−O(8) 93.3(2), C−Ga−Ga 157.6 (av), O−Ga−Ga 88.0 (av), Ga−O−C 119.3 (av), O−C−O 125.1 (av).

Scheme 2



4

A byproduct of the reaction according to eq 1 (**4**) was detected by NMR spectroscopy. Its concentration strongly increases to a 2:1 ratio (**3** to **4**) when the reaction was carried out in *n*-hexane instead of THF. Former observations confirmed that polar solvents favor the substituent exchange reaction upon treatment of **1** with acids, while nonpolar solvents favor the cleavage of the Ga−Ga bond. Owing to the integration ratio of the ^1H NMR spectrum, compound **4** was formed by the oxidation of the Ga atoms and contains two dialkylgallium groups per one dicarboxylato ligand as schematically shown in Scheme 2. Recrystallization from methylcyclopentane afforded a few single crystals of **4**. Crystal structure determination verified that the carboxylato groups do not occupy bridging positions between two Ga atoms but are terminally coordinated in a chelating manner to only one Ga atom (Figure 2). This is a quite unusual and unexpected structure, because generally dialkylgallium(III) carboxylates[9,10] and their aluminum

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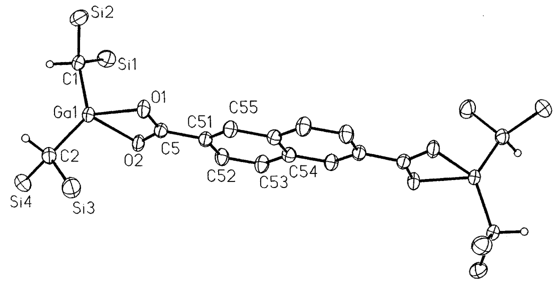

Figure 2. Molecular structure of **4**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups and hydrogen atoms of the naphthalene bridge are omitted for clarity. Important bond lengths (Å) and angles (deg): Ga(1)−C(1) 196.2(3), Ga(1)−C(2) 196.0(3), Ga(1)−O(1) 204.2(2), Ga(1)−O(2) 205.6(2), C(1)−Ga(1)−C(2) 131.3(1), O(1)−Ga1−O(2) 64.53(8), Ga(1)−O(1)−C(5) 88.9(2), Ga(1)−O(2)−C(5) 88.5(2), O(1)−C(5)−O(2) 118.0(3).

homologues[11,12] form dimers with both carboxylato ligands bridging both Ga or Al atoms. The preference of that particular structure was partially explained by the inflexibility of the O−C−O angle.[6,12] For the bridging group an angle of 125° was calculated by ab initio methods, which is in close agreement with angles found in digallium compounds with and without Ga−Ga bonds. Furthermore, this value is close to that calculated for the free formiate anion (129°). The terminal arrangement of a carboxylato group results in a deformation of that angle to 117° (118.0° observed in **4**). Additionally, the close transannular contact between the inner C atom and the Ga atom (239.0 pm in **4**) disfavors those structures by steric and electrostatic repulsion. Overall, the terminal arrangement of a carboxylato group was calculated to be 117 kJ mol^{-1} less favorable than the bridging one. In contrast, the triatomic triazenido ligand [R−NNN−R]$^-$, possessing a lone pair of electrons at its inner N atom, prefers the terminal coordination to gallium.[13] The angle at the inner N atom can easily be deformed to lower values, which is favorable for a terminal coordination (106° observed for gallium triazenido compounds), and a much lower charge separation leads to a diminished transannular electrostatic repulsion. The unusual structure of **4** may be caused by the steric shielding of the Ga atoms by two bulky substituents. The bridging of two bulky GaR_2 moieties [R = $CH(SiMe_3)_2$] by only one carboxylato ligand was reported for the compound $(R_2Ga)_2(\mu\text{-}O_2CR')(\mu\text{-}OH)$, in which the second bridging position was occupied by a small hydroxy group.[14] The ring strain in the GaO_2C heterocycle results in relatively long Ga−O distances of 204.9 pm (av) compared to 201.4 pm (av) in the bridged species **3**.

Table 1. Crystal Data, Data Collection Parameters, and Structure Refinement Details for Compounds 3 and 4

	3 ($\cdot 8C_6F_2H_4$)	**4** ($\cdot 2MeC_5H_9$)
formula	$C_{152}H_{176}F_8Ga_8O_{16}Si_{16}$	$C_{52}H_{106}Ga_2O_4Si_8$
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)[16]	$P2_1/n$ (No. 14)[16]
Z	1	2
temp, K	193(2)	193(2)
D_{calcd}, g/cm^3	1.233	1.117
a, Å	14.124(1)	9.6188(8)
b, Å	17.805(1)	17.8307(9)
c, Å	20.020(2)	20.315(1)
α, deg	90.266(6)	90
β, deg	105.679(6)	98.378(9)
γ, deg	107.488(6)	90
V, 10^{-30} m^3	4603.0(6)	3447.1(4)
μ, mm^{-1}	1.315	0.903
cryst dimens, mm	0.5 × 0.3 × 0.3	0.4 × 0.4 × 0.3
radiation	Mo Kα; graphite-monochromator	
θ range, deg	1.53−26.18	2.23−25.96
index ranges	$-17 \leq h \leq 17$ $-22 \leq k \leq 21$ $-24 \leq l \leq 24$	$-11 \leq h \leq 11$ $-21 \leq k \leq 21$ $-22 \leq l \leq 24$
no. of unique reflns	17 938 [R_{int} = 0.0622]	6683 [R_{int} = 0.0654]
no. of params	713	281
R1 (reflns $I > 2\sigma(I)$)	0.0725 (11328)	0.0421 (4333)
wR2 (all data)	0.2198	0.0979
max./min. residual electron density, 10^{30} e/m^3	1.009/−0.809	0.668/−0.492

Experimental Section

All procedures were carried out under purified argon. Cyclopentane and methylcyclopentane were dried over $LiAlH_4$; THF over Na/benzophenone; and 1,2-difluorobenzene over molecular sieves. Digallane(4) **1** was obtained by a literature procedure.[4] Commercially available naphthalene-2,6-dicarboxylic acid was employed without further purification.

Synthesis of *cyclo*-Tetrakis{(*μ*-naphthalene-2,6-dicarboxylato-*O,O'*)-1,2-bis[bis(trimethylsilyl)methyl]digallium(*Ga−Ga*)}, 3. Digallane(4) **1** (0.278 g, 0.359 mmol) was dissolved in 40 mL of THF and cooled to 0 °C. The yellow solution was treated with solid naphthalene-2,6-dicarboxylic acid (0.076 g, 0.352 mmol) in small portions. The mixture was warmed to room temperature and stirred for 18 h. The solvent was removed in a vacuum, and the pale yellow residue was thoroughly evacuated. It was dissolved in 10 mL of cyclopentane and filtered. After concentration the solution was cooled to −70 °C to obtain a pale yellow solid of **3**. Yield: 0.185 g (77%). Mp (argon, sealed capillary): **3** does not melt at <380 °C; a darkening of the solid was observed at >300 °C. Anal. Calcd for $C_{104}H_{176}O_{16}Si_{16}Ga_8$ (2689.7): C, 46.4; H, 6.6. Found: C, 46.9; H, 6.8. ^{1}H NMR (C_6D_6, 300 MHz): δ 8.61 (8 H, s, 1,5-H of naphthyl), 8.15 (8 H, d, $^3J_{H\cdots H}$ = 8.8 Hz, 3,7-H of naphthyl), 7.33 (8 H, d, $^3J_{H\cdots H}$ = 8.8 Hz, 4,8-H of naphthyl), 0.46 (144 H, s, $SiMe_3$), −0.01 (8 H, s, Ga−CH). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 177.1 (CO_2), 135.1 (ipso-C of naphthyl), 132.4, 130.6, 130.2, and 126.7 (naphthyl), 5.1 (GaC), 3.5 ($SiMe_3$). IR (CsBr plates, paraffin, cm^{-1}): 1603 vw (naphthyl); 1547 vw, 1418 m $\nu(CO_2)$; 1464 vs, 1377 vs (paraffin); 1306 m, 1258 w, 1248 m $\delta(CH_3)$; 1200 m, 1140 sh, 1080 vs, 1047 vs ν(CC), δ(CH); 1013 s $\delta(CHSi_2)$; 922 s, 885 m, 843 s, 795 m, 789 m, 758 w, 721 s $\rho(CH_3(Si))$; 673 vw, 669 w ν_{as}(SiC); 627 w ν_s(SiC); 515 vs, 467 vs ν(GaO), ν(GaC); 345 w, 303 vw δ(SiC).

Characterization of (*μ*-Naphthalene-1,6-dicarboxylato-*O,O'*)-bis{bis[bis(trimethylsilyl)methyl]gallium}, 4. The reaction according to eq 1 in *n*-hexane instead of THF yielded 2:1 (**3** to **4**) mixtures of products. Recrystallization of the rough product from methylcyclopentane (20/−30 °C) afforded small quantities of solid **4**. Mp (argon, sealed capillary): 218 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ 8.68 (2 H, s, 1,5-H of naphthyl), 8.08

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(2 H, d, $^3J_{\text{H}\cdots\text{H}}$ = 8.5 Hz, 3,7-H of naphthyl), 7.28 (2 H, d, $^3J_{\text{H}\cdots\text{H}}$ = 8.5 Hz, 4,8-H of naphthyl), 0.30 (72 H, s, $SiMe_3$), −0.23 (4 H, s, GaCH). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 181.5 (CO_2), 132.3, 130.9, 129.5, and 126.5 (naphthyl), 11.1 (GaC), 3.9 ($SiMe_3$). IR (CsBr plates, paraffin, cm^{-1}): 1597 m (naphthyl); 1530 s, 1479 sh $\nu(CO_2)$; 454 vs, 1377 vs (paraffin); 1360 s, 1302 m, 1260 s, 1248 vs $\delta(CH_3)$; 1196 m, 1181 w, 1140 w, 1103 w, 1076 w ν(CC); 1020 vs δ(CH); 968 s, 953 s, 922 m, 841 vs, 787 vs, 760 s, 723 m $\rho(CH_3(Si))$; 691 m, 671 s ν_{as}(SiC); 644 m, 623 m, 615 m ν_s(SiC); 548 w, 509 s, 476 s ν(GaO),ν(GaC); 380 vw, 355 w, 338 vw δ(SiC).

Crystal Structure Determinations of 3 and 4. Single crystals of **3** were obtained by recrystallization from a saturated solution in 1,2-difluorobenzene (20/+4 °C). The macrocycles reside on crystallographic inversion centers. Eight molecules of the solvent are enclosed in the crystals per each formula unit of **3**. Some of these show a severe disorder; in these cases, only the six-membered ring was refined with restrictions of structural parameters. Single crystals of compound **4** were obtained by recrystallization of a rough product of the reaction in hexane (see above) from methylcyclopentane (20/−30 °C). A crystallographic inversion center is located on the inner C−C bond of the naphthalene bridge. Two molecules of the solvent are enclosed per each formula unit of **4**. The crystallographic data of both compounds were collected with a STOE image plate diffractometer. The structure was solved by direct methods and refined with the program SHELXL-97[15] by a full-matrix least-squares method based on F^2. Crystal data, data collection parameters, and structure refinement details are given in Table 1. Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC-219673 (**3**) and -219674 (**4**).

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Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic displacement parameters, and all bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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