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A Molecular Box with an Edge Length of 1.5 nm: Four Ga−Ga Bonds Bridged by Dicarboxylato and Hydroxo Ligands

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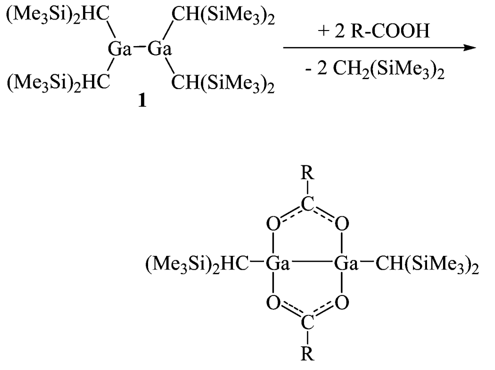
Summary: The four Ga−Ga bonds of the title compound **2** *are bridged by two 4,4′-biphenyldicarboxylato and four hydroxo ligands to yield a molecular box with an edge length of 1.5 nm.* **2** *was obtained by treatment of the digallium compound* $R_2Ga-GaR_2$ *(**1**; R = CH(SiMe₃)₂) with 4,4′-biphenyldicarboxylic acid in the presence of water.*

Introduction

In contrast to the Al−Al[1,2] or In−In[2,3] single bonds of organoelement dialuminum or diindium compounds, the Ga−Ga bond of the corresponding tetraalkyldigallane(4) $R_2Ga-GaR_2$ ($R = CH(SiMe_3)_2$)[4] shows remarkable resistance to attack of protic reagents. Thus, treatment of **1** with 2 equiv of a carboxylic acid resulted in the formation of bis(trimethylsilyl)methane and gave the corresponding dicarboxylatodigallium compound in which the Ga−Ga bond was retained and bridged by the carboxylato ligands (eq 1).[5−8] The chelating groups adopted an ideally perpendicular arrangement, and the C−Ga−Ga−C skeleton of the molecules approached linearity. By this particular preorganization these structures favored the formation of a macrocyclic derivative, when **1** was treated with 1 equiv of a dicarboxylic acid. Depending on the rigidity of the organic backbones of the dicarboxylate thus formed, two different structural motifs were found which contain two[9] or four Ga−Ga bonds.[10] Large squaric heterocycles were obtained by this route, possessing a diameter of the central cavity of up to 1.9 nm. Schematic drawings of two examples are depicted in Chart 1. These compounds resemble in some respect the porous metal−organic framework materials formed with transition-metal atoms which have found considerable interest in recent research.[11] By accident we isolated a compound which had different bridging ligands between its Ga−Ga bonds. This product and its specific synthesis are described here.



(1)

R = -CH₃, -C₆H₅, -4-Br-C₆H₄, -CMe₃, -3,5-C₆H₃Me₂, -Adamantyl

Results and Discussion

The reactions of the digallium(4) compound **1** with carboxylic acids are rather sensitive toward traces of moisture. They are usually performed in thoroughly dried solvents, and the acids are sublimed under vacuum or at least thoroughly evacuated prior to use. In the case of 4,4′-biphenyldicarboxylic acid on one occasion we observed the formation of an unexpected byproduct (**2**), which could be isolated in small quantity by recrystallization. It was characterized initially by ^1H NMR spectroscopy. The trimethylsilyl groups showed two resonances of equal intensity (δ 0.429 and 0.433). The splitting may be caused by a chiral surrounding of the metal atoms and has been detected before.[5,7] The protons of the GaCH groups resonated at a relatively high field (δ −0.27), which is indicative of a coordination number of 4 at the gallium atoms[12] (for comparison, δ 1.09 for **1**[4]). A characteristic AB spectrum was observed for the protons attached to the biphenyl skeleton (δ 6.64 and 7.84). There was an additional resonance of lower intensity (δ 2.64), which we assigned to hydroxo groups. This shift is similar to that of $\{[(Me_3Si)_2CH]_2GaOH\}_2$ (δ 1.78).[13] The integration of the ^1H NMR spectrum revealed a ratio of two alkyl groups, one biphenylene spacer, and two hydroxo groups. This inspired us to synthesize this particular product on purpose by treatment of digallane(4) **1** with 1 equiv of water and $^1/_2$ equiv of 4,4′-

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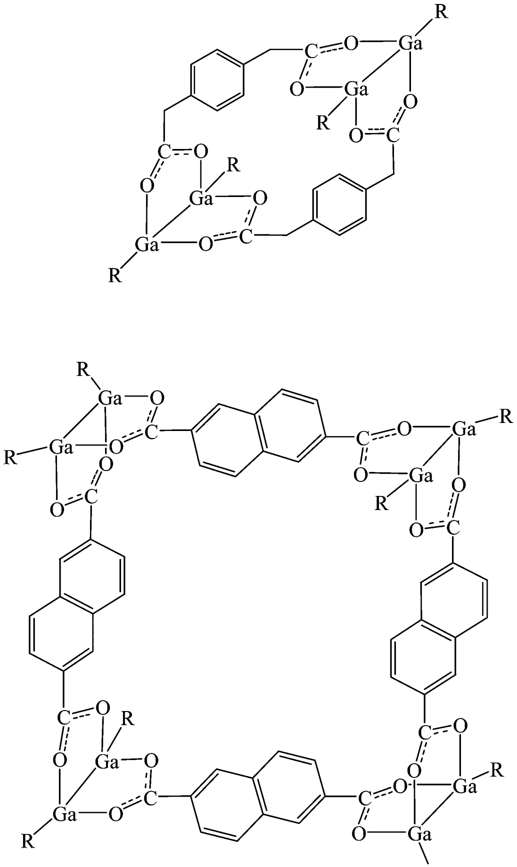
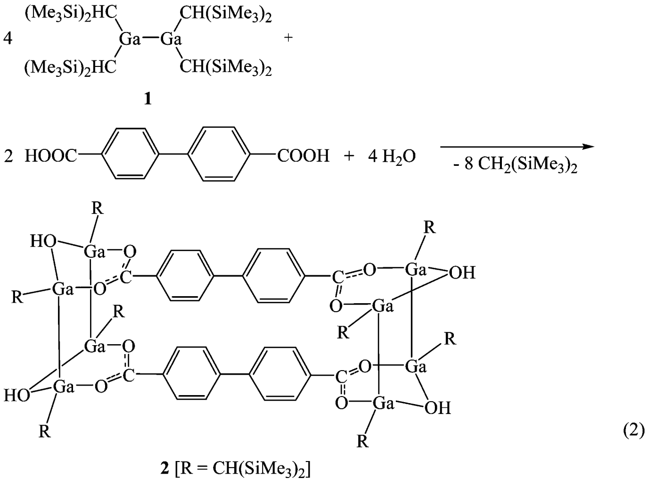
10.1021/om0607954 CCC: $33.50

Chart 1. Schematic Drawings of Two Macrocyclic Compounds Bridged by Ga−Ga Bonds[9,10c]



[R = CH(SiMe$_3$)$_2$]

biphenyldicarboxylic acid. We did not expect a successful reaction course, because in an earlier investigation we showed that water cleaved the Ga−Ga bond of **1**, giving the corresponding dialkylgallium hydroxide in 51% yield.[8]



1

2 [R = CH(SiMe$_3$)$_2$]

(2)

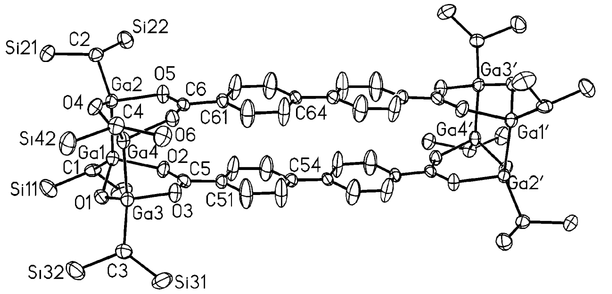


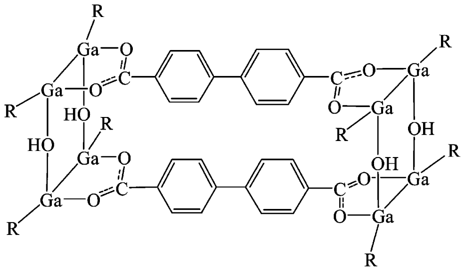
Figure 1. Molecular structure of **2**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups and hydrogen atoms are omitted for clarity. Only the main molecule is shown (see text). The atoms Si(12) and Si(41) are not named. Important bond lengths (Å) and angles (deg): Ga(1)−Ga(2) = 2.448(1), Ga(3)−Ga(4) = 2.454(1), Ga(1)−O(1) = 1.932(3), Ga(1)−O(2) = 2.011(3), Ga(2)−O(4) = 1.936(3), Ga(2)−O(5)′ = 1.999(3), Ga(3)−O(1) = 1.947(3), Ga(3)−O(3) = 1.984(3), Ga(4)−O(4) = 1.928(3), Ga(4)−O(6)′ = 2.004(3); Ga−O−Ga = 117.9 (av), Ga−Ga−O(carboxylate) = 103.4 (av), Ga−Ga−C = 131.4 (av). The atoms Ga(1)′, Ga(2)′, Ga(3)′, Ga(4)′, O(5)′ and O(6)′ were generated by $-x + 2$, $-y + 2$, $-z$.

Polar solvents favor substituent exchange, while in some cases cleavage of the Ga−Ga bond is preferred in hydrocarbon medium.[10] Thus, the reaction was carried out in THF solution. An emulsion of the dicarboxylic acid and water in THF was homogenized in an ultrasound bath for 15 min prior to its addition to a cooled (0 °C) THF solution of **1** (eq 2). The mixture was slowly warmed to room temperature. The solvent was removed under vacuum, and the residue was treated with benzene. A voluminous colorless solid precipitated, which was filtered. It was insoluble in common solvents (pentane to acetonitrile), and its constitution remained unknown. Benzene was removed from the filtrate, and the residue was recrystallized from *n*-hexane or toluene to give compound **2** in 31% yield. The NMR data are in complete agreement with those described above, and thus, the compound accidentally formed by traces of water as described before was reproduced by a specific route according to eq 2.

The constitution of **2** was clarified by an X-ray crystal structure determination (Figure 1). A unique and unprecedented structure was observed, which makes an important contribution to the class of macrocyclic compounds derived from the digallium compound **1**. A flat macrocycle was formed, comprising four Ga−Ga bonds, two biphenyldicarboxylato ligands, and four hydroxo groups. Two RGa−GaR units are bridged by two hydroxo groups to give a six-membered Ga_4O_2 heterocycle in a boat conformation. In all cases characterized so far, the carboxylato groups were in a bridging position across the Ga−Ga bonds (Chart 1). Another structure is adopted in the present case, in which the carboxylato ligands are bonded to two gallium atoms of different Ga−Ga bonds. Thus, a second type of heterocycle results which contains two gallium atoms of different Ga_2 units, a bridging hydroxo group, and the chelating CO_2 ligand. Two of these tricyclic systems are connected by two parallel biphenylene spacers. The angles Ga−Ga−O, including the oxygen atoms of the carbonyl groups, are 102.2−104.4°, and the aromatic rings are almost ideally coplanar with an angle between their normals of only 2.9°. An almost ideally rectangular molecular box results which has edge lengths of 1.49 nm (Ga1−Ga4′) and 1.50 nm (Ga2−Ga3′) along the biphenylene spacers. The distance between the phenyl groups is about 3.60−3.65 Å (C51−C61′; C54−C64′), which corresponds to a normal van der Waals distance. The Ga−Ga bond lengths are 2.451 Å on average, which is longer than the bridged bonds in other carboxylatodigallium species (about 2.38 Å). Compound **2** crystallizes with two mesitylene molecules per formula unit. The solvent molecules are located perpendicular to the biphenyl planes and cover the open sides of the boxes. They fill the hollows between the bulky substituents of both halves of the molecule.

A remarkable disorder of the Ga−Ga units occurred in the solid state. In addition to the main component just described, a second set of gallium positions could be refined belonging to

Chart 2. Minor Component in the Crystal Structure of 2



[R = CH(SiMe$_3$)$_2$]

another minor species with a different molecular structure. The occupation factors are 90 and 10%. In the minor component each Ga−Ga bond is bridged by a carboxylato ligand, which resembles the situation normally observed for digallium dicarboxylates. That particular bridging causes a shortening of the Ga−Ga bond to 2.362 Å on average, which is close to the value characteristic of these systems. A schematic drawing of the second structure is given in Chart 2. The synthesis of compound **2** may open a route for the generation of even larger macrocycles containing parallel strands of organic spacers. The close contact of the spacer ligands should result in a relatively fixed conformation and may contribute to the stability and an improvement of the crystallization behavior of those compounds.

Experimental Section

All procedures were carried out under purified argon. *n*-Hexane and benzene were dried over LiAlH$_4$ and THF and mesitylene over Na/benzophenone. The digallium compound **1** was obtained according to a literature procedure.[4] 4,4′-Biphenyldicarboxylic acid (Aldrich) was thoroughly evacuated (10^{-3} Torr) prior to use.

Synthesis of 2. 4,4′-Biphenyldicarboxylic acid (0.064 g, 0.264 mmol) and 9.4 μL of demineralized water (0.0094 g, 0.522 mmol) were treated with 15 mL of THF. The suspension was homogenized in an ultrasound bath for 15 min. It was added to a cooled (0 °C) solution of the digallium compound **1** (0.405 g, 0.522 mmol) in 50 mL of THF. The mixture was slowly warmed to room temperature and stirred for 16 h in the dark. All volatiles were removed under vacuum at room temperature, and the residue was thoroughly evacuated to remove the byproduct bis(trimethylsilyl)methane. The residue was treated with 50 mL of benzene, which yielded a suspension containing a voluminous, waxy, and colorless solid. The solid was filtered off. Evaporation of the filtrate yielded a colorless solid material which was recrystallized from hexane (or toluene) (+20/−15 °C). Yield: 0.104 g (31%); **1** crystallized with two molecules of *n*-hexane per formula unit. Mp (argon, sealed capillary): compound **2** does not melt until 360 °C. Anal. Calcd for **2** ($C_{84}H_{172}Ga_8Si_{16}O_{12}\cdot 2C_6H_{14}$; 2553.7): C, 45.1; H, 7.8; Ga, 21.8. Found: C, 44.8; H, 7.8; Ga, 20.9. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.84 (8 H, d, $^3J_{HH} = 7.6$ Hz, phenyl), 7.09 (8 H, d, $^3J_{HH} = 7.6$ Hz, phenyl), 2.64 (4 H, s, OH), 1.24 (16 H, s, CH$_2$ of *n*-hexane), 0.88 (12 H, pseudo-t, CH$_3$ of *n*-hexane), 0.433 and 0.429 (each 72 H, s, SiMe$_3$), −0.27 (8 H, s, GaCH). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.61 (8 H, d, $^3J_{HH} = 8.4$ Hz, phenyl), 7.09 (8 H, d, $^3J_{HH} = 8.4$ Hz, phenyl), 2.30 (4 H, s, OH), 1.29 (16 H, s, CH$_2$ of *n*-hexane), 0.90 (12 H, pseudo-t, CH$_3$ of *n*-hexane), 0.15 and 0.16 (each 72 H, s, SiMe$_3$), −0.58 (8 H, s, GaCH). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 174.1 (CO$_2$), 144.4, 131.6, 130.5, and 126.7 (aromatic rings), 31.7, 27.7, and 14.1 (*n*-hexane), 9.3 (GaC), 3.8 and 3.7 (SiMe$_3$). IR (CsBr plates, paraffin, cm^{-1}): 3626 w ν(OH); 2957 vs, 2920 vs, 2854 vs paraffin; 1610 w, 1582 s, 1535 m phenyl, ν(CO$_2$); 1460 vs (paraffin); 1413 s δ(CH); 1377 s (paraffin); 1301 vw, 1259 m, 1245 s δ(CH$_3$); 1015 m δ(CHSi$_2$); 954 w, 842 vs, 776 w, 759 m ρ(CH$_3$Si); 731 w (paraffin); 672 ν_{as}(SiC); 616 vw ν_s(SiC); 591 vw, 525 vw, 510 vw, 483 w ν(GaC); ν(GaO).

Table 1. Crystal Data, Data Collection Parameters, and Structure Refinement Details for 2·2(1,3,5-Me$_3$C$_6$H$_3$)

formula	$C_{102}H_{196}Ga_8O_{12}Si_{16}$
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)[15]
Z	1
temp, K	193(2)
D_{calcd}, g/cm^3	1.264
a, Å	12.802(3)
b, Å	14.112(3)
c, Å	20.178(4)
α, deg	74.87(3)
β, deg	82.51(3)
γ, deg	79.28(3)
V, 10^{-30} m^3	3445(1)
μ, mm^{-1}	1.726
cryst dimens, mm	0.36 × 0.24 × 0.03
radiation	Mo Kα; graphite monochromator
θ range, deg	1.51 − 26.22
index ranges	$-15 \le h \le 15$ $-17 \le k \le 17$ $-23 \le l \le 25$
no. of unique rflns	13 782 ($R_{int} = 0.0565$)
no. of params	682
R1 (rflns $I > 2\sigma(I)$)	0.0438 (8413)
wR2 (all data)	0.1289
max/min residual electron density, 10^{30} e/m^3	0.765/−0.647

Crystal Structure Determination of 2·2(1,3,5-Me$_3$C$_6$H$_3$). Single crystals of **2** are difficult to generate. Xylene and mesitylene proved to be suitable solvents. The crystal structure determination discussed here was conducted with a crystal obtained by recrystallization from mesitylene upon very slow cooling from +20 to −15 °C over 1 week. The crystals enclose two mesitylene molecules per formula unit of **2**. The crystallographic data were collected with a STOE IPDS diffractometer. The structure was solved by direct methods and refined with the program SHELXL-97[14] 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. The molecules of **2** reside on crystallographic centers of symmetry. The gallium atoms and the oxygen atoms of the hydroxo groups show a disorder. A detailed discussion is given in the text. Further details of the crystal structure determination are available from the Cambridge Crystallographic Data Center on quoting the depository number CCDC-619396 (**2**).

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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.

OM0607954

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