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Full Paper

Macrocyclic Gallium Compounds

Ga–Ga Bonds as Key Building Blocks for the Formation of Supramolecular Entities – Unusual Macrocyclic Tetra- and Octagallium Compounds

Werner Uhl,*[a] Christina Stefaniak,[a] and Marcus Layh[a]

Dedicated to Professor Evamarie Hey-Hawkins on the occasion of her 60th birthday

Abstract: Treatment of the digallium compound $R_2Ga–GaR_2$ (**1**) [R = $CH(SiMe_3)_2$] with the dicarboxylic acids 1,2- and 1,4-$(HO_2CCH_2O)_2C_6H_4$ afforded, by the release of $H_2C(SiMe_3)_2$, macrocyclic compounds **2a** and **2c**, in which two organic spacer ligands connect two metal–metal bonds. Two CO_2 groups bridge each Ga–Ga bond, and different structures resulted with a parallel or perpendicular arrangement of the bridging ligands. The resorcinol derivative 1,3-$(HO_2CCH_2O)_2C_6H_4$ yielded the unique compound **2b**, in which four Ga–Ga bonds are bridged by four spacer ligands. The organic groups form loops, which are alternately arranged above and below the molecular plane with four saddle points and a structure approaching $\bar{4}$ symmetry. The 1,2- and 1,4-diacids afforded tetrakis(digallium) compounds **3a** and **3c** in the presence of water. In both cases carboxylate groups and hydroxido ligands bridge two Ga atoms of two different Ga–Ga bonds. The spacer ligands connect two of these fragments and adopt parallel orientations to form molecular boxes. Again, the 1,3-diacid afforded a unique structural motif in which a Ga_4O_6 skeleton (two Ga–Ga bonds) is bridged by a single organic spacer, reminiscent of the handle of a basket.

Introduction

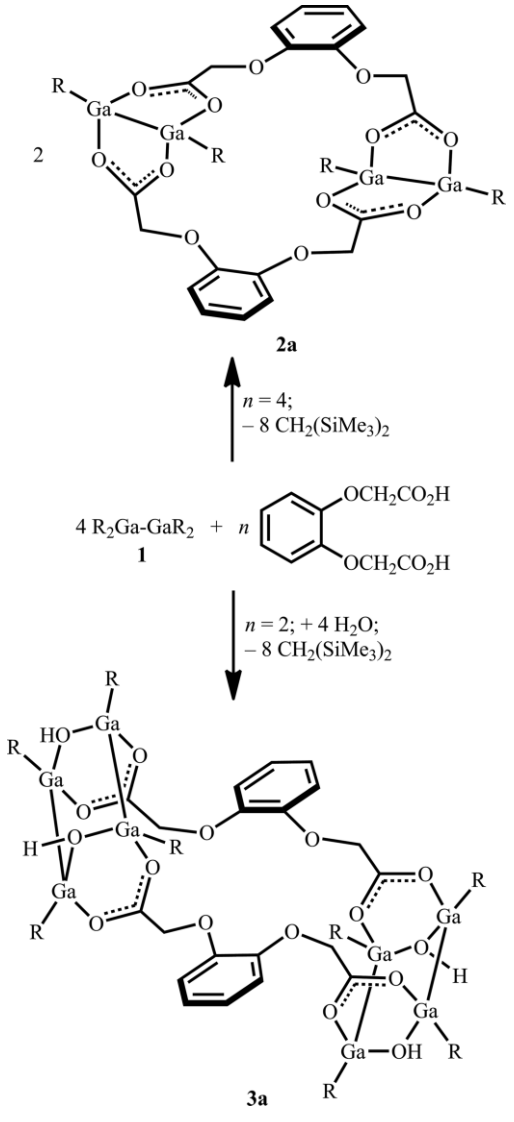
Macrocyclic and cage-like compounds in which metal atoms are bridged by suitable organic spacer ligands are an important area in current research.[1] These compounds show fascinating supramolecular properties and are potentially applicable for the storage of small molecules or as reaction cavities. Transition metals were generally used for the generation of such compounds,[1] but recently it has been shown that Ga–Ga single bonds are similarly effective for the formation of macrocycles and cages.[2] These oligogallium compounds were formed by the highly selective reaction of bifunctional carboxylic acids with the digallium compound $R_2Ga–GaR_2$ [**1**; R = $CH(SiMe_3)_2$].[3] While the Ga–Ga bond was retained in these reactions, the corresponding dialuminium[4] and diindium compounds[5] exclusively reacted by cleavage of the M–M bonds (M = Al, In) and oxidation of the metal atoms.[6] Treatment of **1** with carboxylic acids resulted in the replacement of two alkyl groups per formula unit of **1** and afforded digallium dicarboxylates in which the chelating ligands bridge the Ga–Ga bonds.[2] The bridging coordination of the CO_2 ligands (formation of Ga_2O_2C heterocycles) is favoured over the terminal arrangement (four-membered GaO_2C rings) as a result of lower electrostatic repulsion between the Ga and carbonyl C atoms.[2,7] These compounds have almost linear Ga–Ga–C moieties, and the carboxylate groups adopt a perpendicular arrangement. Both structural features have been rationalised by the presence of formally sp-hybridised Ga atoms.[2,7] The sp-hybridised orbitals are used for the formation of Ga–C and Ga–Ga bonds, while the Ga–O bonds are essentially based on the p orbitals at Ga. The resulting structural motif is perfectly preorganised for the generation of macrocycles with two or four Ga–Ga bonds. The latter compounds adopt a quadratic arrangement of parallel Ga–Ga bonds, and the resulting heterocycles have inner diameters of up to 1.9 nm.[8] Nitrogen- or hydroxy-functionalised carboxylic acids yielded three-dimensional cages with three to six digallium groups in a single molecule.[9–11] These compounds show supramolecular chemistry with the formation of carcerands,[9,11] the coordination of molecules by hydrogen bonding,[10] orthogonal dipolar interactions[12] and sulfur–sulfur closed-shell interactions.[13] Hydroxido–carboxylato-bridged digallium compounds (molecular boxes) were obtained by the reaction of **1** with oligofunctional carboxylic acids in the presence of water.[14] Unexpectedly, water did not result in complete decomposition of the organogallium compounds. In continuation of this work, we treated **1** with the bifunctional dicarboxylic acids $C_6H_4(OCH_2COOH)_2$, which allowed easy modification of the spacer properties by means of different positions of the functional groups at the phenylene ring (*ortho*, *meta* and *para*) and are derived from catechol, resorcinol and hydroquinone.

[a] *Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstrasse 30, 48149 Münster, Germany*
E-mail: uhlw@uni-muenster.de
www.uni-muenster.de/chemie.ac/uhl/index.html
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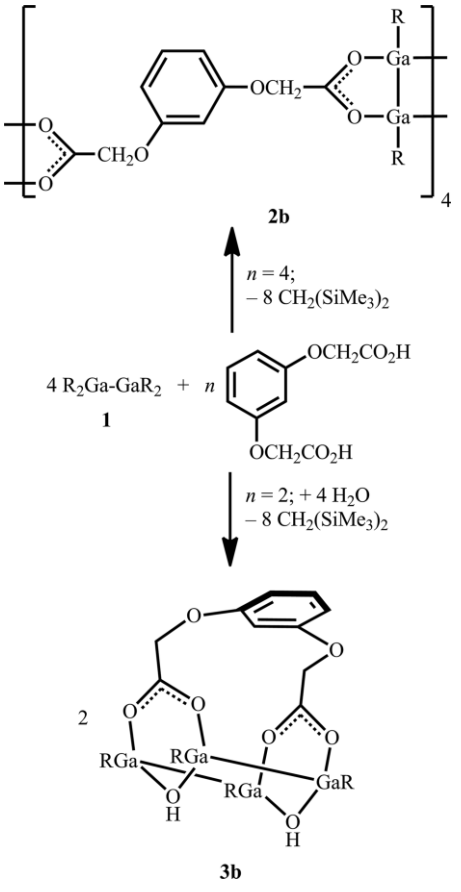
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Results and Discussion

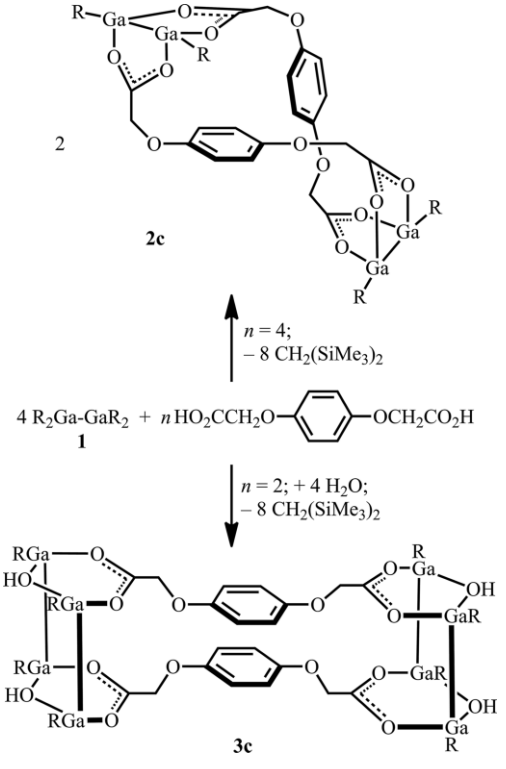
Treatment of solutions of the yellow digallium compound $R_2Ga–GaR_2$ [**1**; R = $CH(SiMe_3)_2$][3] in THF at room temperature with equimolar quantities of the dicarboxylic acids 1,2-, 1,3- and 1,4-$(HOOCCH_2O)_2C_6H_4$ (Schemes 1, 2 and 3) yielded mixtures which gradually changed colour from yellow to colourless. The colour change indicated the consumption of **1** and the formation of new products with four-coordinate Ga atoms. After stirring overnight and removal of the solvent in vacuo, compounds **2** were obtained as colourless oils. A small excess (ca. 10 %) of the dicarboxylic acids was required for complete transformation of **1**. The acids reacted by Ga–C bond cleavage and release of two molecules of $H_2C(SiMe_3)_2$ per formula unit of **1**. The Ga–Ga bond was retained, and compounds **2a**–**c** were formed in selective reactions. The mixed hydroxido–carboxylato compounds **3** were obtained as colourless oils (**3a**, **3b**) or a solid material (**3c**) with a similar selectivity when the stoichiometric ratio of **1**



Scheme 1. Reactions of **1** with 1,2-$(HOOCCH_2O)_2C_6H_4$ in the absence and presence of water [R = $CH(SiMe_3)_2$].



Scheme 2. Reactions of **1** with 1,3-$(HOOCCH_2O)_2C_6H_4$ in the absence and presence of water [R = $CH(SiMe_3)_2$].



Scheme 3. Reactions of **1** with 1,4-$(HOOCCH_2O)_2C_6H_4$ in the absence and presence of water [R = $CH(SiMe_3)_2$].

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to dicarboxylic acid was changed to 2:1 and water was added (ca. 1.2 equiv. based on **1**; Schemes 1, 2 and 3). Water acted as a single-proton donor to replace a bis(trimethylsilyl)methyl substituent by a bridging hydroxo group. A second alkyl group was exchanged by a carboxylate ligand (Schemes 1, 2, and 3), and the Ga–Ga bond remained intact. An excess of water (≈ 20 %) was favourable to increase the yields. All compounds were directly formed in high purity and showed only minor impurities in the NMR spectra. Recrystallisation from *n*-pentane (**2a–c**, **3a**, **3c**) or 1,2-dimethoxyethane (**3b**) afforded single crystals suitable for X-ray analysis, but only in the cases of **2b**, **3b** and **3c** was it possible to obtain more than a few crystals, with yields of 42, 47 and 87 %, respectively. The yields of 84–96 % given in the Experimental Section for the remaining compounds are based on the crude products. The crystalline compounds are thermally fairly stable with melting or decomposition points of 77 °C for the 1,2-derivative **3a**, 120–140 °C for the 1,3 derivatives (**2b**, **3b**) and 200–240 °C for **2a** and the 1,4-derivatives (**2c**, **3c**).

Compounds **2a–c** form macrocycles in which each RGa–GaR fragment [R = $CH(SiMe_3)_2$] is coordinated by the organic spacer ligands through two carboxylate groups. The CO_2 groups bridge the Ga–Ga bonds through both O atoms to form two five-membered Ga_2O_2C heterocycles, which adopt a perpendicular arrangement (Figures 1, 2 and 3). In compounds **3a–c** the additional OH groups cause a dramatic change of the basic structural motif. The two O atoms of the carboxylato ligands are now coordinated to Ga atoms of two different RGa–GaR moieties (Figures 4, 5 and 6). The same two Ga atoms are further bridged by an OH group, and this results in six-membered $CO_2Ga_2O(H)$ heterocycles that adopt a distorted envelope conformation. The intact Ga–Ga bonds lead to a parallel arrangement of two of these six-membered heterocycles with a distance that corresponds to the length of the Ga–Ga bonds.

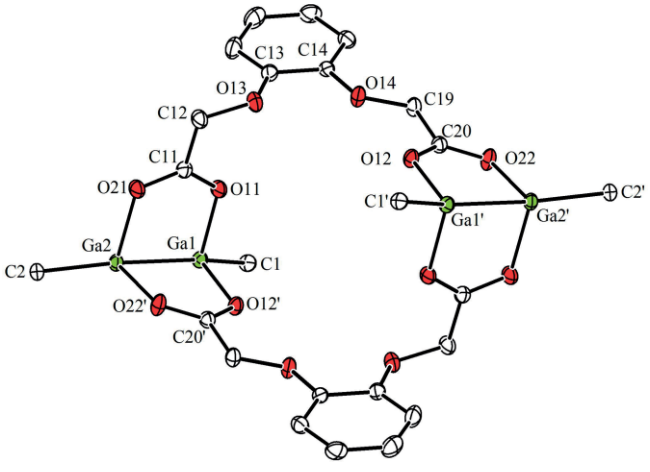


Figure 1. Molecular structure of **2a**. Displacement ellipsoids are drawn at 40 % probability. $SiMe_3$ groups and hydrogen atoms are omitted for clarity; equivalent atoms generated by $-x + 2, -y, -z + 1$.

Selected bond lengths and angles of compounds **2a–c** are summarised in Table 1. The Ga–Ga bond lengths deviate only slightly from the average value of 238 pm for the standard

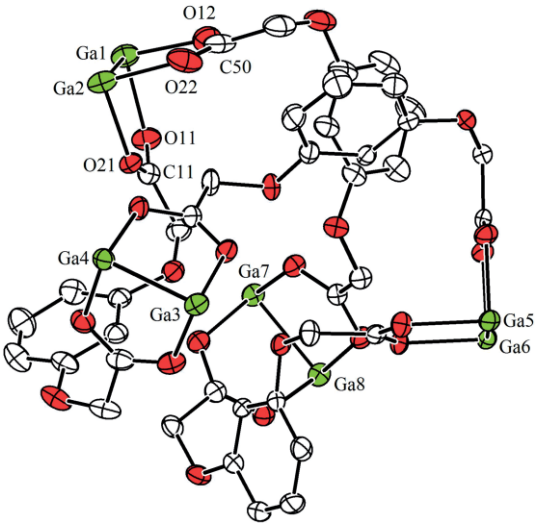


Figure 2. Molecular structure of **2b**. Displacement ellipsoids are drawn at 40 % probability. $CH(SiMe_3)_2$ groups and hydrogen atoms are omitted for clarity.

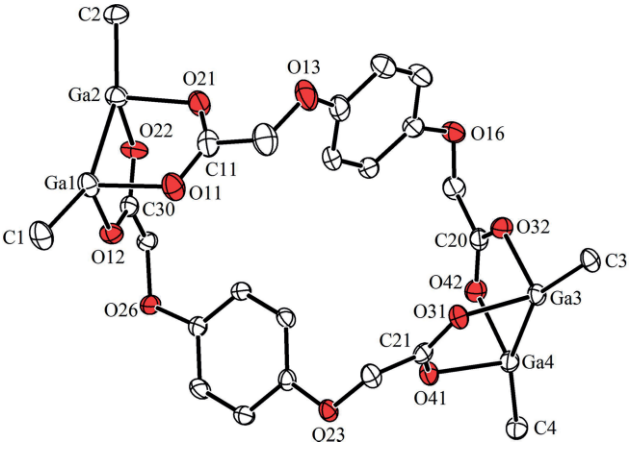


Figure 3. Molecular structure of **2c**. Displacement ellipsoids are drawn at 40 % probability. $SiMe_3$ groups and hydrogen atoms are omitted for clarity.

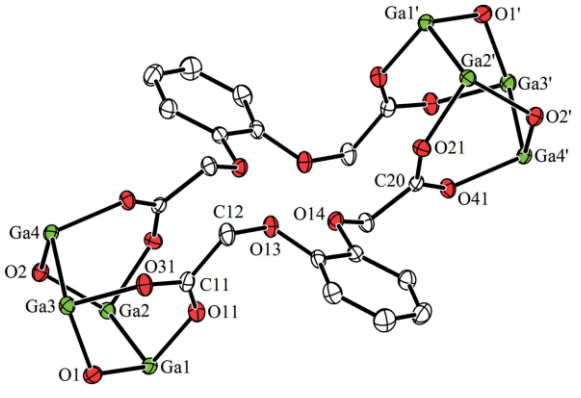


Figure 4. Molecular structure of **3a**. Displacement ellipsoids are drawn at 40 % probability. $CH(SiMe_3)_2$ groups and hydrogen atoms are omitted for clarity; equivalent atoms generated by $-x + 1, -y, -z + 1$.

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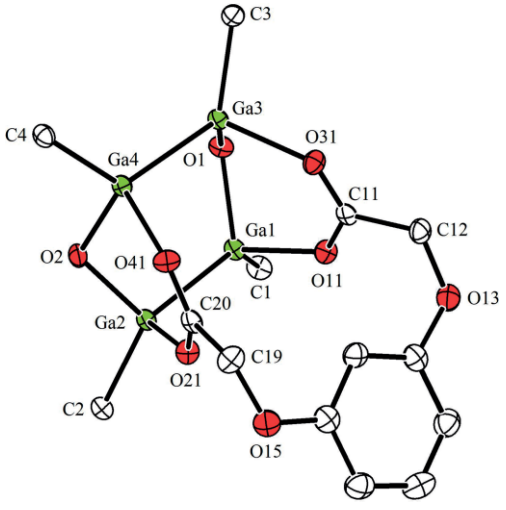


Figure 5. Molecular structure of **3b**. Displacement ellipsoids are drawn at 40 % probability. $SiMe_3$ groups and hydrogen atoms are omitted for clarity.

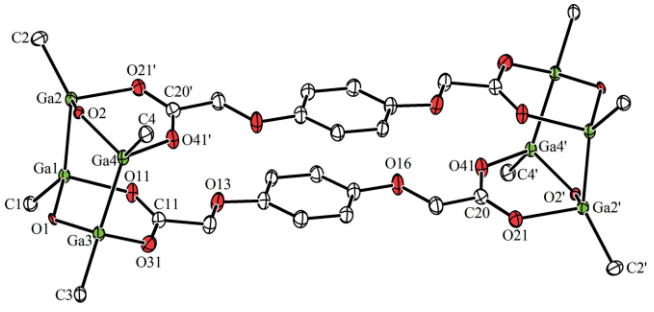


Figure 6. Molecular structure of **3c**. Displacement ellipsoids are drawn at 40 % probability. $SiMe_3$ groups and hydrogen atoms are omitted for clarity; equivalent atoms generated by $-x + 1, -y + 1, -z + 1$.

bond lengths in comparable compounds.[7–14] They are significantly shorter than those observed in the starting compound **1** [254.1(1) pm][3] and the OH-bridged compounds **3a**–**c** (244 pm on average).[14] The short bonds in **2a**–**c** and the unusual perpendicular arrangement of the chelating ligands are both caused by the relatively small bite of the chelating CO_2 group (distance between the coordinating O atoms: 225 pm) which forces a short distance between the Ga atoms. Further details of bonding and structures are discussed in the Introduction. Hybridisation and the unfavourable bite angle may explain the comparatively long Ga–O distances (202 pm on average).

In compounds **3a**–**c**, the carboxylate and hydroxido ligands bridge two different RGa–GaR fragments (Figures 4, 5 and 6). Consequently, the Ga–Ga bonds are significantly lengthened (244 pm) and the angles at Ga including the C–Ga–Ga angles (< 137°) approach values expected for a distorted tetrahedral coordination of the Ga atoms (Table 1). The Ga–O distances of 198.4–201.0 pm (Ga–OCO) and about 194 pm (Ga–OH) are significantly shorter, and the Ga–C bond lengths of 198 pm longer, than those in compounds **2a**–**c**. The C–O bond lengths in the carboxylate groups are similar in all compounds and consistent with delocalisation of π-electron density. The general trends in both types of compounds are comparable to those of related macrocycles.[8–14]

Despite the similarity of angles and distances to those of previously published compounds, **2** and **3** show unprecedented molecular structures. In **2a** the carboxylate groups are in the 1,2-positions of the phenylene ring. It forms a centrosymmetric dimer with 22 atoms in the heterocycle (Figure 1). The 15 heavy atoms of a $[H_2COC_6H_4OCH_2CO_2Ga_2]$ fragment including the phenylene ring, one carboxylate group and a Ga–Ga bond are approximately in a plane (largest deviation from the average plane: 34 pm for O22) and parallel to the centrosymmetric counterpart. The two planes are linked by coordinative bonding of two carboxylate groups to Ga–Ga bonds (angle CO_2Ga_2/Ga_2O_2C ca. 90°, Table 1), creating an open molecular box with edge lengths of 433 (distance between the two $[COC_6H_4OCH_2CO_2Ga_2]$ planes) and 567 pm (distance between CO_2Ga_2 planes of opposite Ga–Ga bonds; Ga1–C14′ 593 pm). These tetragallium compounds are connected into molecular stacks by weak supramolecular interactions between OCH_2 groups of different molecules (O···H 260 pm; O···C 342 pm). The related hydroxido-bridged compound **3a** (Figure 4) is a centrosymmetric tetrakis(digallium) compound, in which four $CO_2Ga_2(OH)$ linkers (see above) are connected by four Ga–Ga bonds and two almost planar COC_6H_4OC groups (largest deviation from plane of 15 pm for C19). The latter groups are coplanar with a distance between the average planes of only 8 pm. The carboxylate groups on both sides of the organic backbone are arranged above and below the two planes with each of the oxygen atoms binding to a Ga atom of different Ga–Ga bonds. These Ga atoms are further bridged by OH groups. The lengths of the edges inside the box are 571 (*o*-C C14···C14′), 1072 (Ga1···Ga4′) and 1139 pm (Ga2···Ga3′). The four ether O atoms bound to the aromatic rings adopt a rhombic arrangement with relatively short intramolecular O···O distances between 255 (O13···O14) and 407 pm (O13···O14′). With this arrangement, compound **3a** may be suitable to act as a chelating ligand for the coordination of cations. The molecules of **3a** are connected into strands by two weak intermolecular

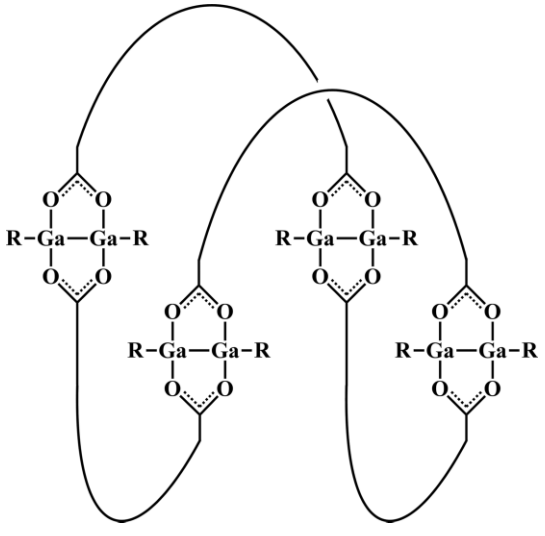
Table 1. Selected bond lengths [pm] and angles [°] of **2a**–**c** and **3a**–**c**.

	2a	**2b**	**2c**	**3a**	**3b**	**3c**
Ga–Ga	237.96(2)	237.53(av)	239.35(av)	244.92(av)	243.25(av)	244.93(av)
Ga–C	195.2(av)	195.4(av)	195.3(av)	198.6(av)	198.0(av)	196.7(av)
Ga–O	201.6(av)	202.0(av)	202.2(av)	201.0(av)	199.6(av)	198.4(av)
Ga–OH	–	–	–	194.1(av)	194.4(av)	193.5(av)
O–C(CO_2)	126.3(av)	126.4(av)	126.6(av)	126.2(av)	125.9(av)	127.1(av)
C–Ga–Ga	157.36(av)	155.4(av)	158.4(av)	127.82(av)	122.18(av)	136.9(av)
O–Ga–O	92.68(av)	90.22(av)	93.94(av)	94.10(av)	93.38(av)	92.7(av)

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interactions between H atoms of the aryl substituents and the corresponding C atoms of the next molecules (H17···C16 288 pm).

When the oxyacetate substituents occupy the 1,3-positions at the phenylene ring the formation of strain-free tetragallium compounds seems no longer possible, and compound **2b** crystallises as an octagallium compound in which four Ga–Ga bonds are bridged by four spacer ligands (Figure 2). The structure-determining features are again essentially planar COC_6H_4OC fragments (largest deviation from plane of 10 pm for C22). The RGa–GaR fragments are coordinated to two carboxylate groups in an approximately perpendicular arrangement. Comparable tetrakis(digallium) compounds have simple, almost planar, macrocycles in which the Ga–Ga bonds occupy the vertices of regular squares with the rigid spacer ligands arranged across the edges. This arrangement results in the formation of large cavities, which were filled by solvent molecules[8c,8d] or the bulky $CH(SiMe_3)_2$ substituents of neighbouring molecules.[8c] Compared to these compounds, **2b** has a complicated and fascinating new structure. The unique behaviour may be caused by the 1,3-positions of the functional groups, which induce an angle of 120° in the backbone, and by the flexibility of the organic spacers, which results essentially from the O atoms and the CH_2 groups. The structure can be described as a folded strand, as schematically shown in Scheme 4. The four Ga–Ga bonds are bridged by four loops, which are formed by the spacer ligands. These loops are alternately arranged above and below the average molecular plane to generate a stationary wave. The molecules approach a situation with a pseudo-$\bar{4}$ axis. Comparable compounds are rare.[15] Tetrameric copper(I) carboxylates have similar structures in which Cu^{I} ions are bridged by carboxylate groups. The loops (Cu–O–C–O–Cu) in these tetranuclear complexes are much shorter than that of the octagallium compound **2b** (3 vs. 11 bridging atoms). Four



Scheme 4. Schematic drawing of the molecular structure of **2b**; for simplicity the organic spacer ligands are represented by lines, and the dicarboxylatodigallium moieties are not drawn with the typical perpendicular arrangement of the bridging CO_2 groups.

ether O atoms of **2b**, one of each bridging ligand, form an O_4 tetrahedron with edge lengths of 353 to 408 pm and angles between 53 and 68°. With this preorganised structure **2b** seems to be well suited to act as a ligand for the coordination of cations.

The 1,3-dicarboxylic acid afforded another unprecedented structure when it was treated with **1** in the presence of water. A tetranuclear $Ga_4(OH)_2$ compound **3b** (Figure 5) was isolated, which is the first example of a molecule with a single dicarboxylate ligand bridging two Ga–Ga bonds. The COC_6H_4OC backbone remains essentially planar (largest deviation from plane: 6 pm for C12). The Ga–Ga bonds are unsupported, and both RGa–GaR fragments are bridged by hydroxo and carboxylate groups, similar to compound **3a**, with each Ga atom of a Ga–Ga bond connected to another CO_2 ligand. The entire structure can be described as a basket formed by the Ga–O framework with the spacer ligand as the handle. Long-range intermolecular CH···C interactions between an H atom of a CH_2 group and the aromatic ring of a neighbouring molecule (H19A···C13 272 pm; H19A···C18 281 pm) result in the formation of weakly bound dimers in the solid state.

Compound **2c** crystallises as a tetragallium compound (Figure 3) comparable to **2a**, but in contrast to **2a** the molecule is folded in such a way that two planar OC_6H_4O fragments (largest deviation from plane: 3 pm for O atoms) are approximately perpendicular to each other (angle between planes: 87°). They are linked by RGa–GaR units, which are bound to carboxylate groups above and below the respective aromatic plane with O–Ga–O angles close to 90°. Several dipolar interactions and short contacts between H atoms and O or C atoms [OCH···O 249 pm, OCH···OCO 258, 261, 269 pm; OCH···C(Ph) 285 pm] of adjacent molecules result in the formation of molecular strands. The OH-bridged compound **3c** crystallises as a centrosymmetric octanuclear macrocycle in which the Ga atoms of four Ga–Ga bonds are bridged by four carboxylate groups of two spacer ligands and four OH groups (Figure 6). The resulting molecular box features two essentially planar COC_6H_4OC groups (largest deviation 5 pm for C18) in a parallel arrangement. The aromatic rings show a ring slippage of about 112 pm. The dimensions of the molecular box can be defined by the distance between the planes of the aromatic rings of 339 pm, which is close to the value of 335 pm found in graphite, the distance between the hydroxido-bridged Ga–Ga fragments (ca. 340 pm) and the distance between Ga atoms across an edge of the box (1470 pm on average).

The resonances of the α-C and α-H atoms of the $CH(SiMe_3)_2$ groups show a significant high-field shift upon formation of the heterocycles, from $\delta = 0.31$ (**1**) to $\delta \approx -0.5$ (**2a–c** and **3a–c**) and from 25.9 (**1**) to about 5 (**2a–c**) or 10 (**3a–c**) in the ^1H and ^{13}C NMR spectra. Comparable effects are observed for the $SiMe_3$ groups [1.11 and 6.9 (**1**) vs. 0.1 and 3.6 (**2a–c**, **3a–c**)]. This is consistent with the increased coordination number of the Ga atoms and the associated increase of electron density at the metal atoms.[16] The effect is less pronounced for the OH derivatives **3a–c** ($CHSi_2$: $\delta = 10$) as compared to **2a–c** ($\delta = 5$), possibly as a result of the harder character of the OH ligand compared to the CO_2 group. There is a small trend in the opposite direc-

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tion in the ^{1}H NMR resonances of the associated protons [(C*H*Si$_2$), δ = –0.40 to –0.48 in **2a**–**c** and δ = –0.50 to –0.60 in **3a**–**c**]. Apart from minor differences in chemical shifts of ^{29}Si NMR resonances [ca. 0.2 (**2a–c**) and –1.0 (**3a–c**)] and the additional OH signals at about δ = 3.6 in the ^{1}H NMR spectra of compounds **3a**–**c**, there are no other major differences between the two classes of compounds. The protons of the CH_2 groups show slightly broadened singlet resonances. The $SiMe_3$ groups of the $CH(SiMe_3)_2$ substituents in compounds **2a**–**c** are equivalent, while in compounds **3a**–**c** two resonances are observed in the ^{1}H, ^{13}C and ^{29}Si NMR spectra. This observation reflects molecular symmetry with a mirror plane in compounds **2a**–**c**, which bisects the Me_3Si–C–$SiMe_3$ angles and generates equivalent $SiMe_3$ groups. In compounds **3a**–**c** the Ga atoms have a chiral coordination sphere and the $SiMe_3$ groups are diastereotopic. The OH groups give characteristic signals around 3600 cm^{-1} in the IR spectra. The EI mass spectra were not really meaningful due to unspecific decomposition reactions of the large molecules upon heating in vacuo.

Conclusions

Ga–Ga bonds are efficient building blocks for the generation of macrocycles and cages, which are formed by the selective reactions of the easily available starting material R_2Ga–GaR_2 [**1**; R = $CH(SiMe_3)_2$] with dicarboxylic acids.[2,7,8] Two alkyl groups of each digallium moiety are replaced by carboxylate ligands, which bridge the Ga–Ga bonds and adopt a perpendicular arrangement. Oxygen- and nitrogen-functionalised carboxylic acids afforded cage compounds with interesting supramolecular properties.[9–11] The acids $(HO_2CCH_2O)_2C_6H_4$ allowed the facile modification of stereochemistry by the arrangement of the acidic groups in *ortho*-, *meta*- or *para* positions. The 1,2 and 1,4 derivatives yielded tetranuclear heterocycles in which two Ga–Ga bonds are bridged by two spacer ligands. These compounds showed an almost parallel (**2a**) or perpendicular (**2c**) orientation of the bridging groups. The 1,3 derivative resulted in the formation of an octanuclear compound in which four Ga–Ga bonds are bridged by four spacer ligands (**2b**). This compound adopted a unique structure in which a folded strand formed by the Ga–Ga bonds and the bridging groups afforded an assembly with four saddle points and a pseudo-$\bar{4}$ axis. The spacer ligands form four loops, which alternately are above and below the average molecular plane. This 1,3 pattern of the acidic groups resulted in the formation of another unprecedented structural motif (**3b**) when **1** was treated with the dicarboxylic acid in the presence of water. The Ga–Ga bond was not cleaved, and a compound was isolated in which two unsupported Ga–Ga bonds are bridged by two hydroxido and two carboxylate ligands. Only one spacer ligand is present, and it bridges with both CO_2 groups. This intramolecular coordination has not been observed previously. The other two dicarboxylic acids afforded molecular boxes in the presence of water, in which four Ga–Ga bonds are bridged by four OH groups and parallel organic ligands (**3a**, **3c**). Compounds **2a** and **2b** have four ether O atoms preorganised for the planar or tetrahedral coordination of cations. Another interesting task for future investigations is donor functionalisation. If these reactions tolerate the presence of donor atoms in or at the organic backbone, they may allow the generation of compounds with great potential in supramolecular chemistry. Molecules with larger cavities may be accessible with spacer ligands that have a longer distance between the carboxylate groups, for instance, in naphthalene derivatives.

Experimental Section

General: All procedures were carried out under an atmosphere of purified argon in dried solvents [*n*-pentane with $LiAlH_4$; THF and 1,2-dimethoxyethane (DME) with Na/benzophenone]. NMR spectra were recorded in [D$_6$]benzene at ambient probe temperature with a Bruker Avance I (^{1}H, 400.13; ^{13}C, 100.6 MHz; ^{29}Si, 79.49 MHz) or Avance III (^{1}H, 400.03; ^{13}C, 100.59 MHz, ^{29}Si, 79.47 MHz) instrument and referenced internally to residual solvent resonances. ^{13}C NMR spectra were all proton-decoupled. Elemental analyses were determined by the microanalytical laboratory of the Westfälische Wilhelms Universität Münster. IR spectra were recorded as paraffin mulls between CsI plates with a Shimadzu Prestige 21 spectrometer. 1,2-, 1,3- and 1,4-$(HOOCCH_2O)_2C_6H_4$ are commercially available, and $Ga_2[CH(SiMe_3)_2]_4$[3] was synthesised according to a literature procedure.

{[1,2-$(O_2CCH_2O)_2C_6H_4$][$(Me_3Si)_2CHGa$-$GaCH(SiMe_3)_2$]}$_2$ (2a): A solution of $Ga_2[CH(SiMe_3)_2]_4$ (**1**; 0.25 g, 0.322 mmol) in THF (25 mL) was treated at room temperature with solid 1,2-$(HO_2CCH_2O)_2C_6H_4$ (0.08 g, 0.354 mmol). The mixture was stirred for 18 h at room temperature, and the colour of the solution changed from yellow to colourless. The volatile substances were removed in vacuo to yield compound **2a** as a colourless oil (0.21 g, 96 % based on **1**). The residue contained $CH_2(SiMe_3)_2$ and an unknown impurity in a concentration <10 % (NMR). Recrystallisation from *n*-pentane at –15 °C afforded few colourless crystals suitable for X-ray crystallography. M.p. (argon, sealed capillary): > 212 °C (decomp.). ^{1}H NMR (400 MHz, [D$_8$]THF, 300 K): δ = 6.87 (m, 4 H, 4,5-C_6H_4), 6.82 (m, 4 H, 3,6-C_6H_4), 4.68 (s, 8 H, OCH_2), 0.08 (s, 72 H, $SiMe_3$), –0.47 (s, 4 H, $CHSi_2$) ppm. ^{13}C NMR (100 MHz, [D$_8$]THF, 300 K): δ = 182.4 (CO), 149.5 [1,2-C(C_6H_4)], 122.6 [3,6-C(C_6H_4)], 116.0 [4,5-C(C_6H_4)], 67.8 (OCH_2), 5.0 ($CHSi_2$), 3.4 ($SiMe_3$) ppm. ^{29}Si (79 MHz, [D$_8$]THF, 300 K): δ = 0.1 ppm. IR (CsI plates, paraffin): $\tilde{\nu}$ = 1925 vw, 1859 vw, 1769 vw, 1667 m, 1649 m, 1595 w, 1576 m, 1501 w ν(CO), ν(CC, Ar); 1454 vs, 1377 s (paraffin); 1341 m, 1308 m, 1248 m δ(CH_3); 1202 m, 1161 w, 1132 w, 1051 m ν(CC), ν(CO); 1013 m δ($CHSi_2$); 961 w, 939 w, 843 m, 773 m ϱ(CH_3Si); 723 m (paraffin); 673 m, 611 m ν(SiC); 511 w, 459 vw, 417 vw ν(GaC), ν(GaO) cm^{-1}.

{[1,2-$(O_2CCH_2O)_2C_6H_4$][$(Me_3Si)_2CHGa$-$GaCH(SiMe_3)_2$]$_2$$(OH)_2$}$_2$ (3a): Solid 1,2-$(HO_2CCH_2O)_2C_6H_4$ (0.03 g, 0.133 mmol) was added at room temperature to a yellow solution of compound **1** (0.22 g, 0.284 mmol) in THF (25 mL). The mixture was stirred until the dicarboxylic acid had dissolved (ca. 5 min). Water was added (6.2 µL, 0.344 mmol) with a micro-syringe and the reaction mixture was stirred overnight to yield a colourless solution. Removal of all volatile substances in vacuo afforded compound **3a** as a colourless oil (0.15 g, 89 % based on **1**). Recrystallisation from *n*-pentane gave a few single crystals suitable for X-ray crystallography and characterisation. M.p. (argon, sealed capillary): 77 °C. $C_{76}H_{172}Ga_8O_{16}Si_{16}$ (2349.33): calcd. C 38.9, H 7.4; found C 38.7, H 7.4. ^{1}H NMR (400 MHz, [D$_8$]THF, 300 K): δ = 7.04 (m, 4 H, 3,6-C_6H_4), 7.00 (m, 4 H, 4,5-C_6H_4),

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4.55 (s, 8 H, OCH_2), 3.78 (s, 2 H, OH), 0.13 and 0.14 (each s, 36 H, $SiMe_3$), –0.53 (s, 8 H, $CHSi_2$) ppm. ^{13}C NMR (100 MHz, [D_8]THF, 300 K): δ = 180.9 (CO), 151.7 [1,2-C(C_6H_4)], 125.5 [4,5-C(C_6H_4)], 123.2 [3,6-C(C_6H_4)], 73.6 (OCH_2), 10.0 ($CHSi_2$), 4.2 and 4.0 ($SiMe_3$) ppm. ^{29}Si (79 MHz, [D_8]THF, 300 K): δ = –0.8 and –1.1 ppm. IR (CsI plates, paraffin): $\tilde{\nu}$ = 3620 w ν(OH), 2951 vs, 2920 vs, 2851 vs, 2723 m, 2669 m (paraffin); 1923 vw, 1869 vw, 1859 vw, 1796 vw, 1647 m, 1635 m, 1624 m, 1580 s, 1560 w, 1503 m ν(CO), ν(CC, Ar); 1456 vs, 1377 vs (paraffin); 1339 s, 1317 m, 1292 sh, 1248 s δ(CH_3); 1206 m, 1157 w, 1126 m, 1053 m ν(CC), ν(CO); 1015 m δ($CHSi_2$); 962 m, 843 vs, 777 m, 758 m, 738 sh ϱ(CH_3Si); 723 m (paraffin); 675 m, 613 w ν(SiC); 542 vw, 509 w, 488 w ν(GaC), ν(GaO) cm^{-1}.

{[1,3-(O_2CCH_2O)$_2C_6H_4$][(Me_3Si)$_2$CHGa-GaCH($SiMe_3$)$_2$]}$_4$ (2b): A solution of compound **1** (0.30 g, 0.387 mmol) and 1,3-(HO_2CCH_2O)$_2C_6H_4$ (0.10 g, 0.442 mmol) in THF (25 mL) was stirred for 17 h at room temperature to afford a colourless solution. All volatiles were removed in vacuo to yield a colourless oil. Recrystallisation from *n*-pentane afforded compound **2b** as a mixture of crystalline and amorphous material (0.11 g, 42 % based on **1**). M.p. (argon, sealed capillary): 141 °C (dec.). $C_{96}H_{184}Ga_8O_{24}Si_{16}$ (2729.64): calcd. C 42.2, H 6.8; found C 42.7, H 7.0. ^1H NMR (400 MHz, [D_8]THF, 300 K): δ = 7.06 [t, $^3J_{HH}$ = 7.8 Hz, 4 H, 5-H(C_6H_4)], 6.45 [d, $^3J_{HH}$ = 7.8 Hz, 8 H, 4,6-H(C_6H_4)], 6.27 [s, 4 H, 2-H(C_6H_4)], 4.59 (s, 16 H, OCH_2), 0.10 (s, 144 H, $SiMe_3$), –0.40 (s, 8 H, $CHSi_2$) ppm. ^{13}C NMR (100 MHz, [D_8]THF, 300 K): δ = 182.3 (CO), 160.2 [1,3-C(C_6H_4)], 130.7 [5-C(C_6H_4)], 109.4 [4,6-C(C_6H_4)], 100.1 [2-C(C_6H_4)], 66.7 (OCH_2), 5.2 ($CHSi_2$), 3.4 ($SiMe_3$) ppm. ^{29}Si (79 MHz, [D_8]THF, 300 K): δ = 0.2 ppm. IR (CsI plates, paraffin): $\tilde{\nu}$ = 1927 vw, 1913 vw, 1871 vw, 1857 vw, 1699 vw, 1647 m, 1597 m, 1578 s ν(CO), ν(CC, Ar); 1460 vs, 1375 vs. (paraffin); 1344 s, 1323 s, 1302 s, 1287 s, 1262 s, 1246 s δ(CH_3); 1180 s, 1153 s, 1094 m, 1078 w, 1063 w ν(CC), ν(CO); 1013 m δ($CHSi_2$); 955 m, 843 s, 756 s ϱ(CH_3Si); 723 s (paraffin); 677 m, 610 w ν(SiC); 588 w, 554 vw, 511 w, 453 vw, 421 vw ν(GaC), ν(GaO) cm^{-1}.

[(1,3-O_2CCH_2O)$_2C_6H_4$][(Me_3Si)$_2$CHGa-GaCH($SiMe_3$)$_2$]$_2$(OH)$_2$ (3b): 1,3-(HO_2CCH_2O)$_2C_6H_4$ (0.057 g, 0.252 mmol) was added to a solution of compound **1** (0.39 g, 0.503 mmol) in THF (40 mL). The solution was stirred for approximately 2 min, and water (11.4 µL, 0.633 mmol) was added. The mixture was stirred overnight, and a colourless solution was obtained. The volatile substances were removed in vacuo to yield a colourless solid, which was washed three times with *n*-pentane (5 mL). Recrystallisation from 1,2-dimethoxyethane at room temperature afforded colourless crystals of compound **3b** (0.14 g, 47 % based on **1**). M.p. (argon, sealed capillary): 123 °C (decomp.) $C_{38}H_{86}Ga_4O_8Si_8$ (1174.66): calcd. C 38.9, H 7.4; found C 38.8, H 7.4. ^1H NMR (400 MHz, [D_8]THF, 300 K): δ = 7.06 [t, $^3J_{HH}$ = 8.2 Hz, 1 H, 5-H(C_6H_4)], 6.44 [dd, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 1.9 Hz, 2 H, 4,6-H(C_6H_4)], 6.03 [t, not resolved, 1 H, 2-H(C_6H_4)], 4.65 (s, 4 H, OCH_2), 3.42 (s, 2 H, OH), 0.09 and 0.08 (each s, 36 H, $SiMe_3$), –0.60 (s, 4 H, $CHSi_2$) ppm. ^{13}C NMR (100 MHz, [D_8]THF, 300 K): δ = 179.0 (CO), 159.2 [1,3-C(C_6H_4)], 130.7 [5-C(C_6H_4)], 110.1 [4,6-C(C_6H_4)], 95.7 [2-C(C_6H_4)], 66.9 (OCH_2), 10.1 ($CHSi_2$), 4.3 and 4.0 ($SiMe_3$) ppm. ^{29}Si (79 MHz, [D_8]THF, 300 K): δ = –1.2 and –0.9 ppm. IR (CsI plates, paraffin): $\tilde{\nu}$ = 3620 w, 3561 w ν(OH), 2953 vs, 2922 vs, 2853 vs, 2723 s, 2670 m (paraffin), 1927 vw, 1670 w, 1630 m, 1597 m, 1582 m, 1559 sh ν(CO), ν(CC, Ar); 1462 vs, 1377 s (paraffin), 1306 m, 1281 m, 1248 s δ(CH_3), 1179 w, 1159 w, 1152 w, 1092 w, 1063 vw ν(CC), ν(CO); 1016 w δ($CHSi_2$), 972 w, 955 w, 935 w, 843 vs, 766 m ϱ(CH_3Si), 723 s (paraffin), 679 w, 652 vw, 637 vw, 613 w ν(SiC), 592 w, 519 w, 507 w, 480 w, 461 w ν(GaC), ν(GaO) cm^{-1}.

{[1,4-(O_2CCH_2O)$_2C_6H_4$][(Me_3Si)$_2$CHGa-GaCH($SiMe_3$)$_2$]}$_2$ (2c): A solution of compound **1** (0.38 g, 0.490 mmol) and 1,4-(HO_2CCH_2O)$_2C_6H_4$ (0.12 g, 0.531 mmol) in THF (50 mL) was stirred for 18 h at room temperature. The colour changed gradually from yellow to colourless. All volatiles were removed in vacuo to yield compound **2c** as a colourless oil (0.28 g, 84 %). Recrystallisation from *n*-pentane at –30 °C afforded a few crystals suitable for X-ray analysis. M.p. (argon, sealed capillary): 198–206 °C (decomp.). $C_{48}H_{92}Ga_4O_{12}Si_8$ (1364.82): calcd. C 42.3, H 6.8; found C 42.8, H 7.0. ^1H NMR (400 MHz, [D_8]THF, 300 K): δ = 6.71 (s, 8 H, C_6H_4), 4.57 (s, 8 H, OCH_2), 0.05 (s, 72 H, $SiMe_3$), –0.48 (s, 2 H, $CHSi_2$) ppm. ^{13}C NMR (100 MHz, [D_8]THF, 300 K): δ = 182.7 (CO), 153.6 [1,4-C(C_6H_4)], 115.3 [2,3,5,6-C(C_6H_4)], 66.7 (OCH_2), 5.0 ($CHSi_2$), 3.3 ($SiMe_3$) ppm. ^{29}Si (79 MHz, [D_8]THF, 300 K): δ = 0.2 ppm. IR (CsI plates, paraffin): $\tilde{\nu}$ = 1929 vw, 1850 vw, 1672 s br, 1578 s br, 1506 s ν(CO), ν(CC, Ar), 1456 vs, 1377 vs. (paraffin), 1341 s, 1306 s, 1248 s δ(CH_3), 1206 s, 1109 w, 1082 m ν(CC), ν(CO), 1015 m δ($CHSi_2$), 972 m, 941 w, 864 s, 843 vs, 777 m, 764 m ϱ(CH_3Si), 723 s (paraffin); 677 m, 646 vw, 611 w ν(SiC), 515 w, 461 w ν(GaC), ν(GaO) cm^{-1}.

{[1,4-(O_2CCH_2O)$_2C_6H_4$][(Me_3Si)$_2$CHGa-GaCH($SiMe_3$)$_2$(OH)]$_2$}$_2$ (3c): A solution of compound **1** (0.49 g, 0.632 mmol) in THF (40 mL) was treated at room temperature with 1,4-(HO_2CCH_2O)$_2C_6H_4$ (0.071 g, 0.314 mmol). The yellow mixture was stirred for 1 min, treated with H_2O (14.1 µL, 0.783 mmol) and further stirred at room temperature. After 30 to 60 min a colourless solid started to precipitate, and after 16 h the suspension was filtered to afford compound **3c** as an analytically pure, colourless solid (0.32 g, 87 %). A small number of crystals suitable for X-ray analysis was obtained by recrystallization of **3c** from a large quantity of *n*-pentane, in which **3c** is only sparingly soluble. M.p. (argon, sealed capillary): 233–248 °C (decomp.). $C_{76}H_{172}Ga_8O_{16}Si_{16}$ (2349.33): calcd. C 38.9, H 7.4; found C 38.5, H 7.4. ^1H NMR (400 MHz, [D_8]THF, 300 K): δ = 6.42 [s, 8 H, 2,3,5,6-H(C_6H_4)], 4.38 (s, 8 H, OCH_2), 3.79 (s, 4 H, OH), 0.17 (s, 144 H, $SiMe_3$), –0.50 (s, 4 H, $CHSi_2$) ppm. ^{13}C NMR (100 MHz, [D_8]THF, 300 K): δ = 178.6 (CO), 151.3 [1,4-C(C_6H_4)], 114.4 [2,3,5,6-C(C_6H_4)], 66.1 (OCH_2), 9.1 ($CHSi_2$), 3.3 and 3.1 ($SiMe_3$) ppm. ^{29}Si (79 MHz, [D_8]THF, 300 K): δ = –0.7 and –1.0 ppm. IR (CsI plates, paraffin): $\tilde{\nu}$ = 3620 m ν(OH), 2967 vs, 2941 vs, 2884 vs, 2870 vs, 2843 vs, 2722 vw, 2669 vw (paraffin), 1921 vw, 1873 vw, 1827 vw, 1796 vw, 1599 vs, 1508 s ν(CO), ν(CC, Ar), 1460 vs, 1377 vs. (paraffin); 1344 s, 1308 w, 1296 w, 1260 s, 1244 vs δ(CH_3), 1227 vs, 1169 vw, 1155 vw, 1099 m, 1086 m ν(CC), ν(CO); 1013 s δ($CHSi_2$), 955 s, 928 w, 835 vs br, 775 s, 755 s ϱ(CH_3Si), 725 m (paraffin); 671 s, 640 vw, 613 m ν(SiC), 594 w, 565 vw, 525 m, 511 w, 484 s, 420 vw ν(GaC), ν(GaO) cm^{-1}.

X-ray Crystallography

Crystals suitable for X-ray crystallography were obtained by recrystallisation from *n*-pentane (**2**, **3a**, **3c**) or 1,2-dimethoxyethane (**3b**). Intensity data were collected with a Bruker Quazar or Bruker Venture diffractometer with multilayer optics and Mo-K_α radiation. Data reduction was carried out with the program SAINT+.[17] The crystal structures were solved by direct methods with SHELXTL.[18] Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full-matrix least-squares calculation based on F^2 with SHELXTL. The H atoms were positioned geometrically and allowed to ride on their respective parent atoms. All compounds, except **3b**, crystallised with heavily disordered *n*-pentane molecules. The atoms of the solvent molecules were refined on split positions for compounds **3a** (0.64:0.36), **2c** (0.52:0.28:0.20) and **3c** (one molecule across an inversion centre). The program SQUEEZE[19] was applied to the structures of **2a** (the found electron number corresponded to two pentane molecules in different voids) and **2b** (2.5 molecules of pentane in the cell). Four $CH(SiMe_3)_2$ groups of compound **2b** were disordered and refined on split positions (central atom C1: 0.81:0.19, C2: 0.49:0.51, C3: 0.92:0.08, C7: 0.77:0.23). A $CH(SiMe_3)_2$ group of **3a** was refined on split positions (0.85:0.15).

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Table 2. Crystal data and structure refinement for compounds **2** and **3**.

	2a	**2b**	**2c**·C_5H_{12}	**3a**·2C_5H_{12}	**3b**	**3c**·C_5H_{12}
Empirical formula	$C_{48}H_{92}Ga_4O_{12}Si_8$	$C_{96}H_{184}Ga_8O_{24}Si_{16}$	$C_{53}H_{104}Ga_4O_{12}Si_8$	$C_{86}H_{196}Ga_8O_{16}Si_{16}$	$C_{38}H_{86}Ga_4O_8Si_8$	$C_{81}H_{184}Ga_8O_{16}Si_{16}$
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
T [K]	153(2)	153(2)	153(2)	153(2)	153(2)	153(2)
a [pm]	1021.25(5)	1998.16(7)	1494.32(8)	1356.7(1)	1212.75(6)	1286.8(1)
b [pm]	1090.03(5)	2078.21(8)	1595.37(7)	1364.2(2)	1388.30(7)	1289.2(1)
c [pm]	1787.61(8)	2123.68(8)	1874.29(9)	2041.8(2)	2036.1(1)	2158.8(2)
α [°]	84.732(1)	90.399(1)	70.368(2)	98.445(3)	100.201(2)	86.774(2)
β [°]	82.121(1)	95.839(1)	67.141(2)	103.664(3)	98.094(2)	88.876(2)
γ [°]	80.667(1)	116.259(1)	84.543(2)	112.698(3)	113.202(2)	61.048(2)
V [nm^3]	1.9401(2)	7.8543(5)	3.8753(3)	3.2660(6)	3.0158(3)	3.1286(5)
Z	1	2	2	1	2	1
$\varrho_{calcd.}$ [g cm^{-3}]	1.168	1.154	1.231	1.268	1.294	1.285
μ [mm^{-1}]	1.540	1.522	1.545	1.818	1.965	1.896
$\theta_{min}/\theta_{max}$ [°]	2.29/29.57	2.67/30.03	2.05/30.08	2.70/27.88	2.81/27.91	2.03/30.11
Independent reflections	10754 [R_{int} = 0.024]	45545 [R_{int} = 0.036]	22429 [R_{int} = 0.034]	15486 [R_{int} = 0.028]	14105 [R_{int} = 0.041]	17636 [R_{int} = 0.040]
Completeness to θ_{max} [%]	98.2	99.8	98.2	99.7	98.9	94.1
Parameters	337	1635	875	646	555	620
$R1$[a] [$I > 2\sigma(I)$]	0.0275	0.0482	0.0438	0.0404	0.0367	0.0675
$wR2$(all data)[b]	0.0797	0.1459	0.0974	0.1000	0.0942	0.1511
Largest diff. peak and hole [e nm^{-3}]	0.492, −0.323	1.374, −1.319	0.828, −0.302	1.715, −0.646	1.295, −1.396	0.953, −0.718

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2]^{1/2}$.

The Ga atoms and OH groups of **3c** showed an interesting disorder. In one of the resulting isomers two Ga atoms of two different Ga–Ga bonds were bridged by the carboxylate ligands, as usually observed for such hydroxido species (see Schemes 1, 2 and 3). The minor component (ratio 0.93:0.07) had the carboxylate group in a bridging position across the Ga–Ga bond, as in compounds **2**. Further crystallographic data are summarised in Table 2.

CCDC 1523944 (for **2a**), 1523945 (for **2b**), 1523946 (for **2c**), 1523947 (for **3a**), 1523948 (for **3b**), and 1523949 (for **3c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Keywords: Gallium · Metal–metal interactions · Macrocycles · Supramolecular chemistry · Bridging ligands

[1] a) D. Fujita, A. Takahashi, S. Sato, M. Fujita, *J. Am. Chem. Soc.* **2011**, *133*, 13317–13319; b) G. H. Clever, S. Tashiro, M. Shionoya, *J. Am. Chem. Soc.* **2010**, *132*, 9973–9975; c) O. Petina, D. Rehder, E. T. K. Haupt, A. Grego, I. A. Weinstock, A. Merca, H. Bögge, J. Szakács, A. Müller, *Angew. Chem. Int. Ed.* **2011**, *50*, 410–414; *Angew. Chem.* **2011**, *123*, 430–434; d) W.-B. Yu, Y.-F. Han, Y.-J. Lin, G.-X. Jin, *Chem. Eur. J.* **2011**, *17*, 1863–1871; e) J. S. Mugridge, R. G. Bergman, K. N. Raymond, *Angew. Chem. Int. Ed.* **2010**, *49*, 3635–3637; *Angew. Chem.* **2010**, *122*, 3717–3719; f) S.-L. Huang, T. S. A. Hor, G.-X. Jin, *Coord. Chem. Rev.* **2017**, *333*, 1–26; g) Y.-F. Han, G.-X. Jin, *Acc. Chem. Res.* **2014**, *47*, 3571–3579.

[2] W. Uhl, *Chem. Soc. Rev.* **2000**, *29*, 259–265.

[3] W. Uhl, M. Layh, T. Hildebrand, *J. Organomet. Chem.* **1989**, *364*, 289–300.

[4] W. Uhl, *Z. Naturforsch. B* **1988**, *43*, 1113–1118.

[5] W. Uhl, M. Layh, W. Hiller, *J. Organomet. Chem.* **1989**, *368*, 139–154.

[6] W. Uhl, R. Graupner, S. Pohl, W. Saak, W. Hiller, M. Neumayer, *Z. Anorg. Allg. Chem.* **1997**, *623*, 883–891.

[7] W. Uhl, T. Spies, R. Koch, *J. Chem. Soc., Dalton Trans.* **1999**, 2385–2391.

[8] a) W. Uhl, T. Spies, W. Saak, *Eur. J. Inorg. Chem.* **1998**, 1661–1665; b) W. Uhl, T. Spies, D. Haase, R. Winter, W. Kaim, *Organometallics* **2000**, *19*, 1128–1131; c) W. Uhl, L. Cuypers, M. Prött, K. Harms, *Polyhedron* **2002**, *21*, 511–518; d) W. Uhl, A.-C. Fick, T. Spies, G. Geiseler, K. Harms, *Organometallics* **2004**, *23*, 72–75.

[9] W. Uhl, M. Voß, J. Müller, K. Seubert, *Chem. Eur. J.* **2011**, *17*, 7852–7857.

[10] W. Uhl, M. Voß, M. Layh, F. Rogel, *Dalton Trans.* **2010**, *39*, 3160–3162.

[11] W. Uhl, C. Stefaniak, M. Voß, M. Layh, F. Rogel, J. Kösters, *Z. Anorg. Allg. Chem.* **2015**, *641*, 253–260.

[12] W. Uhl, C. Stefaniak, M. Voß, J. Kösters, F. Rogel, *Organometallics* **2012**, *31*, 6988–6994.

[13] W. Uhl, C. Stefaniak, A. Hepp, J. Kösters, *Eur. J. Inorg. Chem.* **2014**, 3521–3526.

[14] a) W. Uhl, H. R. Bock, A. Hepp, F. Rogel, M. Voß, *Z. Anorg. Allg. Chem.* **2010**, *636*, 1255–1262; b) W. Uhl, E. Er, *Organometallics* **2006**, *25*, 5832–5834; c) W. Uhl, M. Voß, H. Luftmann, *Chem. Commun.* **2009**, 6854–6856.

[15] Some recent examples of tetrameric Cu^{I} carboxylates: a) O. Hietsoi, C. Dubceac, A. S. Filatov, M. A. Petrukhina, *J. Cluster Sci.* **2012**, *23*, 811–821; b) O. Hietsoi, A. S. Filatov, C. Dubceac, M. A. Petrukhina, *Dalton Trans.* **2011**, *40*, 8598–8603; c) A. S. Filatov, O. Hietsoi, Y. Sevryugina, N. N. Gerasimchuk, M. A. Petrukhina, *Inorg. Chem.* **2010**, *49*, 1626–1633; d) Y. Sevryugina, M. Petrukhina, *Eur. J. Inorg. Chem.* **2008**, 219–229; e) Y. Sevryugina, O. Hietsoi, M. Petrukhina, *Chem. Commun.* **2007**, 3853–3855; a related structure was found for a Ge^{II} dicarboxylate: f) V. N. Khrustalev, I. A. Portnyagin, N. N. Zemlyanski, I. V. Borisova, Y. A. Ustynyuk, M. Y. Antipin, M. S. Nechaev, R. West, *Appl. Organomet. Chem.* **2005**, *19*, 774–777; g) a Pd compound: M. Wakioka, Y. Nakamura, Q. Wang, F. Ozawa, *Organometallics* **2012**, *31*, 4810–4816.

[16] a) W. Uhl, T. Spies, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1059–1064; b) W. Uhl, M. Prött, *Z. Anorg. Allg. Chem.* **2002**, *628*, 2259–2263; c) W. Uhl, M. Prött, G. Geiseler, K. Harms, *Z. Naturforsch. B* **2002**, *57*, 141–144; d) W. Uhl, M. R.

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Halvagar, M. Layh, *Chem. Commun.* **2009**, 4269–4271; e) W. Uhl, M. R. Halvagar, M. Claesener, *Chem. Eur. J.* **2009**, *15*, 11298–11306.
[17] *SAINT+*; Version 6.02 (includes *XPREP* and *SADABS*), Bruker AXS INC., Madison, Wisconsin, USA, **1999**; G. M. Sheldrick, *SADABS*, University of Göttingen, Germany, **1996**.
[18] a) *SHELXTL-Plus*, REL. 4.1; Siemens Analytical X-RAY Instruments Inc., Madison, WI, **1990**; b) Sheldrick, G. M. *SHELXL-97*, Program for the Refinement of Structures, University of Göttingen, Germany, **1997**; c) G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
[19] a) P. van der Sluis, A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, 194–201; b) A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13.

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