

## Tetra-tert-Butyl-di- $\mu$ -Hydroxo Digallium(III) and 1,12-Diaza-3,4:9,10-Dibenzo-5,8-Dioxo-cyclo-Pentadecane. Structure and Isomers of the Coordination Compound.

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**Abstract:** Tri-*t*-butylgallium has been reacted with the macrocycle 1,12-diaza-3,4:9,10-dibenzo-5,8-dioxocyclopentadecane which could be a potential ligand for gallium(III). A reaction product was analyzed and single crystal X-ray diffraction experiments showed that it consisted of the cyclic dimer of di-*t*-butylgallium-hydroxide hydrogen bonded to the macrocycle. Without a co-crystallized organic molecule di-*t*-butylgallium hydroxide crystallizes as a trimer. Density functional calculations have been used to predict the structures and the total energies for the monomer, dimer, trimer, and tetramer of dimethylgallium hydroxide in order to provide a basis for the understanding of oligomer population for the dimethylgallium hydroxides. Force field calculations are shown to be able to produce a similar strain energy difference for dimer, trimer, and tetramer forms of (CH<sub>3</sub>)<sub>2</sub>Ga(OH) and this method can economically be used for larger alkyl groups. The force field computations show that the trimeric di-*t*-butyl gallium(III) hydroxide is much

more stable than the dimeric form which therefore must owe its existence to the association with the hydrogen-bonded macrocycle.

**Keywords:** Di-*tert*-butylgallium hydroxide, Dimethylgallium hydroxide, DFT, molecular geometry, force field calculations, isomer stabilization, crystal structure.

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## 1. Introduction

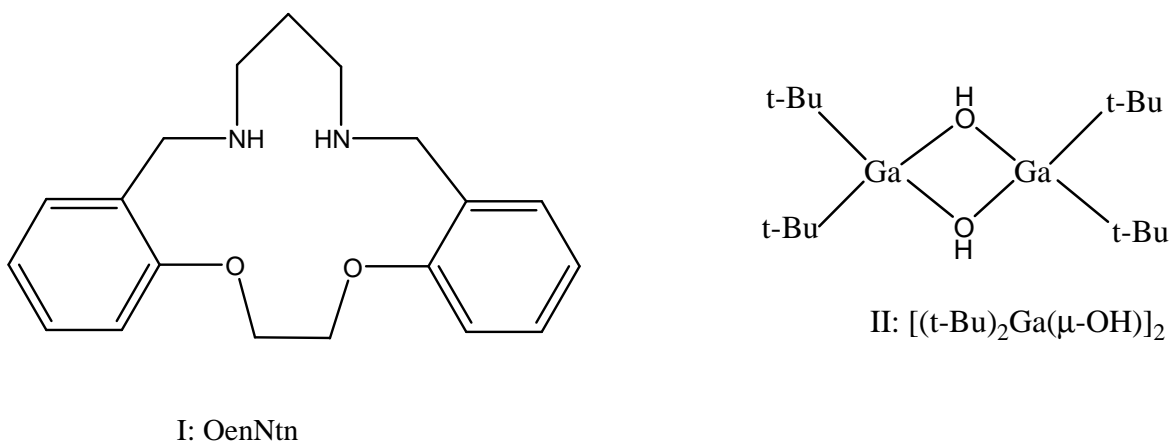
There is a great interest in the chemistry of group 13 organometallic compounds [1-6]. The interest is partly due to their potential use as precursors for organometallic chemical vapor deposition (OMCVD) [7,8]. But the reactions of tri-alkyl aluminum and gallium are also of interest in the study of alumoxanes and galloxanes of the general formula  $(R-M-O)_n$  ( $M = Al, Ga$ ). This group of compounds has in recent years been a target of several investigations into the formation of methylalumoxane (MAO). MAO is used as a component of highly active catalysts for the polymerization of ethylene and propylene [9-12]. The chemical reactivity of MAO has hindered its characterization by NMR spectroscopy. The molecules undergo disproportionation reactions at high temperature and in solution a series of association products is formed to give a mixture of oligomers with multiple equilibria [12]. So far the inability to isolate crystalline samples has prevented characterization by X-ray diffraction. From analytical and phase separation data a three-dimensional cage structure has been inferred but the structure of MAO remains ambiguous and the study of hydrolysis products of alkyl substituted group 13 metal ions thus remains of great interest.<sup>10</sup> Early on it was found that hydrolysis of trimethylgallium with water yields a cyclic dimethylgallium hydroxide tetramer,  $[Me_2Ga(\mu-OH)]_4$ , in the solid phase [13,14]. There has been some discussion of whether the tetramer or smaller oligomers are predominant in equilibrium dominated solutions as this question is only answered by very precise measurements [15,16]. More recently the cyclic trimer  $[t-Bu_2Ga(\mu-OH)]_3$  has been described [17-19], and several examples of hydroxo bridged organogallium dimers have been reported  $[(C_6H_4-o-CH_2NMe_2)_2Ga(\mu-OH)]_2$ ,  $[(CH(SiMe_3)_2Ga(\mu-OH)]_2$ ,  $[(Me_3C_6H_2)_2Ga(\mu-OH)]_2$  [20-22]. The nature of the alkyl substituent on gallium apparently can determine which oligomer is formed in the solid phase, but the presence of a co-crystallizing agent can also influence the nature of the products. In an earlier paper one of us reported on the unexpected reaction products from the reaction between  $Me_3Ga$  and the macrocycles 1,12,15-triaza-3,4:9,10-dibenzo-5,8-dioxacycloheptadecane and 1,12-diaza-3,4:9,10-dibenzo-5,8-dioxacyclopenta-decane (OenNtn) [23]. These compounds represented the first examples of hydrogen bonded cyclic tetrameric and trimeric gallium hydroxide compounds with N/O mixed-donor macrocyclic ethers. Subsequently there have been reports of the addition products  $\{[Me_2Ga(\mu-OH)]\}_3 \cdot 3H_2O$ , 8-crown-6, and  $[(C_6H_5)_2Ga(\mu-OH)]_2 \cdot 3THF$ , as well as the dimer  $[(i-Pr)_2Ga(\mu-OH)]_2$  hydrogen bonded to 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane macro-cycle [24-26]. In the present

communication we describe a hydrogen bonded reaction product composed by OenNtn (I), and the cyclic dimer  $[(t\text{-Bu})_2\text{Ga}(\mu\text{-OH})_2]_2$  (II) (Scheme1). The crystal structure of this adduct has been determined by X-ray diffraction methods. Furthermore the factors that determine the degree of association of  $\mu$ -hydroxodialkylgallium compounds are explored by theoretical calculations based on density functional and molecular mechanical methods.

## 2. Results and discussion

### Synthesis and property of the title compound, $[(t\text{-Bu})_2\text{Ga}(\mu\text{-OH})_2\text{Ga}(t\text{-Bu})_2] \cdot 2 [\text{OenNtn}]$

Dissolution of I with  $(t\text{-Bu})_3\text{Ga}$  in benzene resulted in the formation of the addition product  $[(t\text{-Bu})_2\text{Ga}(\mu\text{-OH})_2\text{Ga}(t\text{-Bu})_2] \cdot 2 [\text{OenNtn}]$  which is stable towards air and moisture only in the solid state. It is readily soluble in benzene and toluene, and it has a moderate solubility in chloroform whereas it does not dissolve in alkanes.



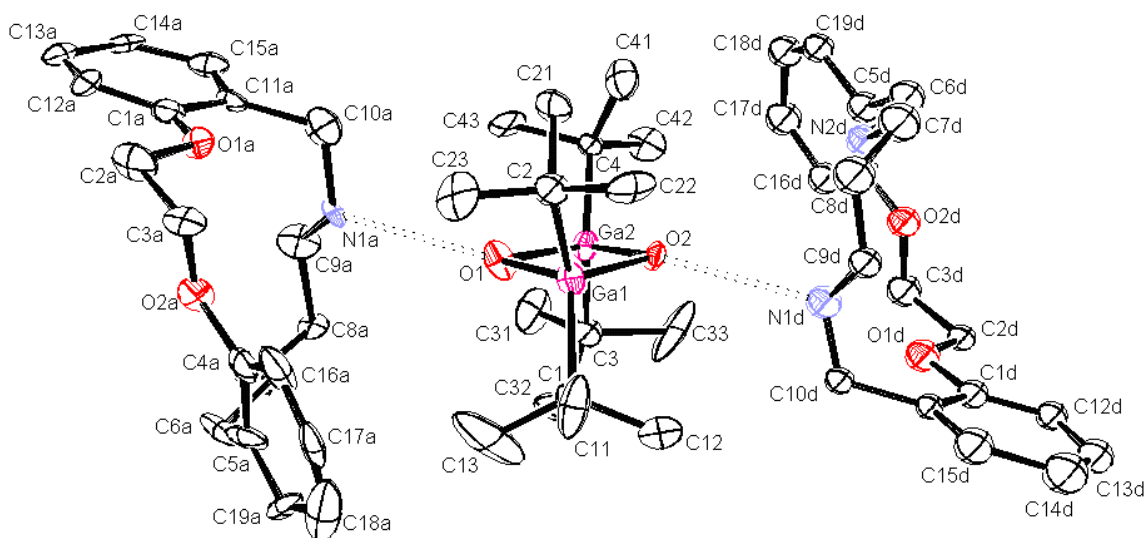
**Scheme 1.** Structural formulas for OenNtn (I) and  $[(t\text{-Bu})_2\text{Ga}(\mu\text{-OH})_2]_2$  (II).

### NMR spectra.

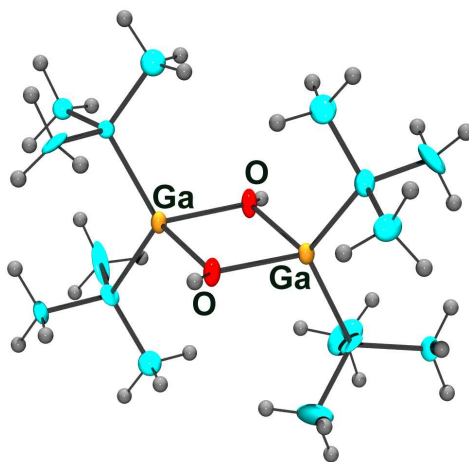
The  $^1\text{H}$  NMR spectra of the complex showed the expected signals at  $\delta$  0.8 ppm for HO and  $\delta$  1.10 ppm for *t*-butyl groups attached to gallium. All peaks can be assigned (see experimental section).

### Description of the crystal structure.

The addition product crystallizes in the triclinic space group P1. The unit cell contains two cyclic dimers of di-*t*-butylgallium hydroxide and four macrocyclic amines. The  $\mu$ -hydroxo bridges donate their protons to the N1 atom of the amine as shown for one pair in the packing diagram, Figure 1, which shows one cyclic dimer of di-*t*-butylgallium hydroxide, and two associated macrocycle units, labeled **a** and **d**. The four donor-acceptor distances are almost identical and are close to 2.8 Å. The molecular structure of the coordination compound is shown in Figure 2.



**Figure 1.** Packing diagram showing the hydrogen bonding interactions for half the interactions in  $[(t\text{-Bu})_2\text{Ga}(\mu\text{-OH})]_2 \cdot 2(\text{OenNtn})$ . The two macrocycle units are labeled **a** and **d**, respectively.



**Figure 2.** Molecular structure of  $[(t\text{-Bu})_2\text{Ga}(\mu\text{-OH})]_2$ . The associated macrocycle units are not shown.

The entities in the unit cell are related by non-crystallographic pseudo symmetry. Each gallium dimer possesses almost an inversion center and the two independent units with their associated macrocycles are related by pseudo translational symmetry of  $(x, \frac{1}{2}+y, \frac{1}{2}+z)$ . It is tempting to assume that the structure could be described by this higher symmetry. However these relations do not reflect an exact non-crystallographic symmetry as the deviations are more than an order of magnitude larger than the standard deviation of the atomic positions, and this explains the failure to refine the structure in P-1. The choice of the acentric space group P1 is supported by the observation that refinement in P1 did not show any correlations between the atoms related by pseudo symmetry

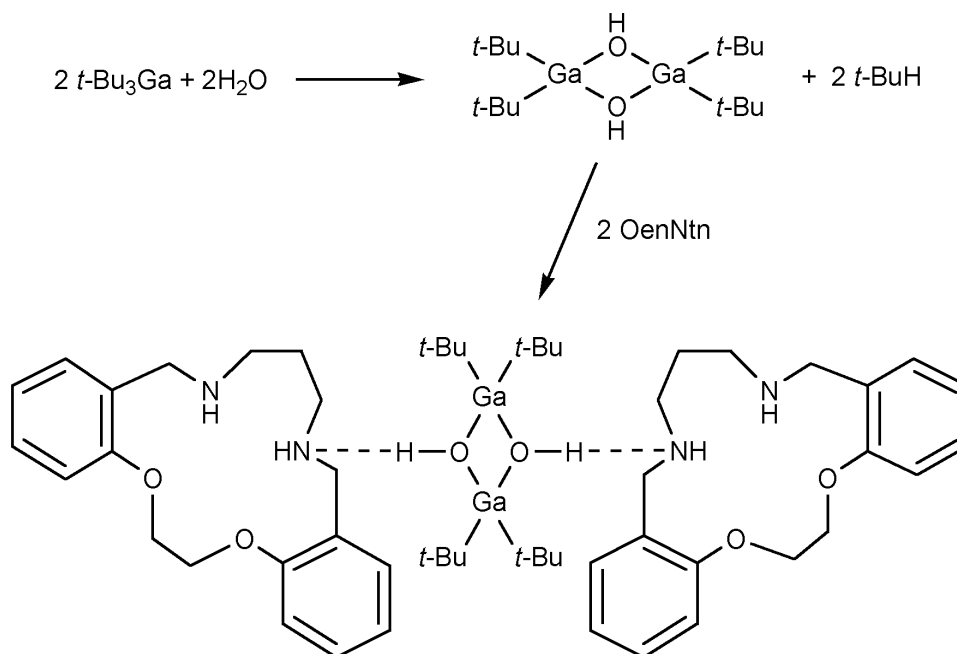
and led also to a reasonable Flack parameter. Within the experimental accuracy the two gallium dimers are identical, and the same holds for the four macrocycles.

The Ga-O distances are in the range 1.922 Å to 1.953 Å with an average value 1.939(18) Å, the Ga-C distances are slightly longer in the range 1.997 Å to 2.031 Å with an average of 2.016(10) Å. Also the bond angles differ slightly with the average values C-Ga-C 118(1)°, while O-Ga-O is only 79.65(15)° and O-Ga-C 113(3)°. Thus, there is a strong angular deviation from tetrahedral symmetry around each gallium ion. This geometry is partly a consequence of the steric requirement exerted by the four bulky *t*-butyl groups. Each ring Ga<sub>2</sub>O<sub>2</sub> ring is planar, and the *t*-Bu ligands attached to the gallium ions are positioned above and below the ring plane. The internuclear distance between the two gallium ions in the dimers is 2.979 (3) Å. The association to the gallium dimer affects the conformation of the macrocycle, and destroys the apparent twofold symmetry around the N1-C10 bond. The torsion angle C9-N1-C10-C11 is around 60° reflecting a *gauche* conformation whereas the conformation of the symmetry related part of the amine N2-C7 is in an *anti* conformation with the C6-N2-C7-C8 torsion angle being close to 180°.

The formation of a 2:1 adduct between macrocycle and dialkyl gallium hydroxide oligomer has been observed in the dimethyl gallium hydroxide by Zhao, et al. [23]; in other cases 1:1 or 1:2 adducts have been isolated [23,24,26]. From the product isolated from the reaction we deduced a reaction sequence where the water resisting total removal is giving rise to the formation of the hydroxide (Scheme 2).

The four distinct OenNtn molecules in the unit cell are all in the same type of endodentate conformation which apparently can facilitate and stabilize the intermolecular hydrogen bonding.

Smaller ring size is favored by the bulky *t*-butyl groups, which could force the angle O-Ga-O' (found to be ~80°) to become smaller than that found for the corresponding trinuclear compound [*t*-Bu<sub>2</sub>Ga(μ-OH)]<sub>3</sub> (~96°) [17-19]. In our case, the formation of an adduct with two hydrogen bonds between [(*t*-Bu)<sub>2</sub>Ga(μ-OH)]<sub>2</sub> and two OenNtn molecules would demand a small Ga-O-Ga angle for making an efficient hydrogen bond.

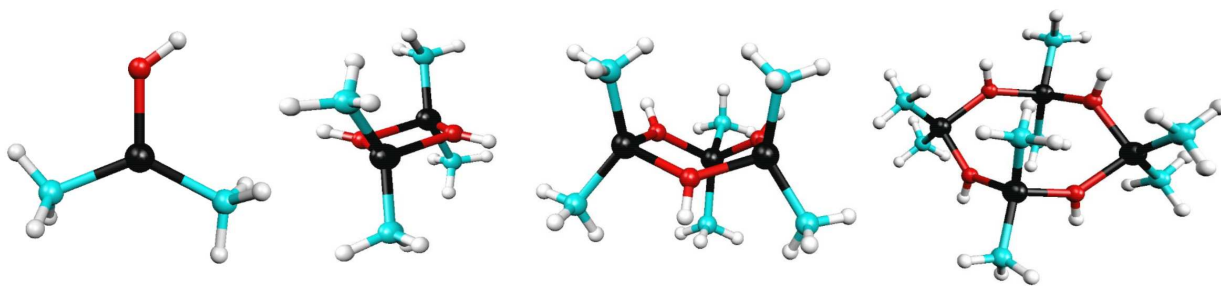


**Scheme 2.** Reaction scheme for the formation of the adduct  $[(t\text{-Bu})_2\text{Ga}(\mu\text{-OH})]_2 \cdot 2 (\text{OenNtn})$ .

In the six-membered ring a larger Ga-O-Ga angle ( $\sim 143^\circ$ ) is needed [18-19], and this should make the oxygen less likely to take part in a strong hydrogen bond. The hydrogen bonding pattern can be considered to mimic the structure of alkoxy-bridged dialkylgallium compounds, which often have been isolated as dimers [17,27-29]. It thus seems likely that the energetically favorable hydrogen bond from  $[(t\text{-Bu})_2\text{Ga}(\mu\text{-OH})]_2$  to the macrocycle is compensating for an unfavorable strain energy in the coordination compound. These considerations fit well with the fact that the Ga-O bonds are slightly longer in the dimer compared to the trimer, which may be due to the repulsion between the two gallium centers in the smaller ring.

### DFT calculations.

By means of density functional theoretical (DFT) calculations the most stable gas phase geometry for each member of the series  $[\text{Me}_2\text{Ga}(\mu\text{-OH})]_n$  ( $n = 1, 2, 3, 4$ ) was computed. The total energy per gallium can be compared relative to the total energy of the monomer. The stability was found to increase with the degree of polymerization, although there was only an insignificant difference in the relative energy between the trimeric and tetrameric forms (Table 1). Illustrations of the predicted geometries are shown in Figure 3, and some important bond lengths and angles are presented in Table 2.



**Figure 3.** Illustration of the  $\text{Me}_2\text{Ga}(\mu\text{-OH})$  oligomer structures optimized by DFT (B3LYP/TZV). From left to right: monomer ( $C_s$ ), dimer ( $C_{2h}$ ), trimer ( $C_s$ ), and tetramer ( $C_{2h}$ ).

**Table 1.** Total self-consistent field (SCF) and relative energies for oligomers of dimethylgallium hydroxide predicted by DFT calculations (B3LYP/TZV).

$[\text{Ga}(\text{Me})_2\text{OH}]_n$	Total SCF energy / Hartree	Relative energy per Ga / kJ/mol
n = 1	-2080.61568481	0
n = 2	-4161.30370289	-95.0
n = 3	-6241.97252808	-109.8
n = 4	-8322.63088554	-110.4

**Table 2.** Selected bond lengths and bond angles for  $[\text{Me}_2\text{Ga}(\mu\text{-OH})]_n$  from DFT calculations (B3LYP/TZV).

	n=1	n=2	n=3	n=4
Ga-O	1.814	1.981	1.973; 1.974	1.970; 1.975
O-H	0.972	0.968	0.972; 0.973	0.974
Ga-C	1.969; 1.983	1.985	1.979 – 1.993	1.977 – 1.993
C-Ga-O	111.3; 117.6	109.1	104.1 – 110.6	103.8 – 109.9
C-Ga-C	131.1	127.7	127.6; 127.9	126.8; 129.1
O-Ga-O	-	77.8	94.8; 96.9	99.6; 99.7
Ga-O-Ga	-	102.2	127.1; 133.8	134.8

The monomeric species was found to be particularly high in total energy. This compound has never been observed, and although the monomeric adduct of  $(t\text{-Bu})_2\text{GaOH}$  with tetrahydrofuran has been reported, the spectroscopic data suggested that THF is bound directly to gallium [17]. Other dimethylgallium compounds have also been found to be at least dimeric, even in the gas phase as seen

for  $[\text{Me}_2\text{Ga}(\mu\text{-X})]_2$  (for  $\text{X}=\text{H}, \text{Cl}$ ) [30]. The DFT calculations show that the most stable geometry for the monomer is of  $\text{C}_s$  symmetry with all four heavy atoms, and the hydroxo and two methyl hydrogen atoms in the mirror plane. Compared to the hydroxo bridged cyclic compounds the Ga-O bond length was more than 0.15 Å shorter implying a double bond character.

The dimer was found to be more stable than the monomer by 95.0 kJ/mol per gallium demonstrating how unfavorable  $\pi$ -bonding is for gallium(III). However, the dimer is still significantly less stable than the trimeric and tetrameric forms of dimethyl gallium hydroxide. To our knowledge the dimer has never been observed experimentally neither naked nor hydrogen bound to another molecule. The final computed molecular geometry was found to conform to the point group symmetry  $\text{C}_{2h}$ . The symmetry plane intersects the  $\text{H-O}\cdots\text{O-H}$  atoms, and the  $\text{C}_2$  axis orthogonal to the plane intersects the gallium atoms. The Ga-O bond length was predicted to be slightly longer than in the higher oligomers, probably a consequence of the short internuclear distance of 3.084 Å between the gallium centers. This computed Ga-Ga distance can be compared to the experimental distance in the corresponding  $[(t\text{-Bu})_2\text{Ga}(\mu\text{-OH})]_2$  of 2.979 Å. The hydrogen atoms of the bridging hydroxo groups are displaced from the  $\text{Ga}_2\text{O}_2$  plane with a O-O-H angle of 161.1°.

The DFT optimization of the geometry for the trimer resulted in a  $\text{C}_s$  symmetrical boat conformation, with a symmetry plane defined by a hydroxo group and the opposing dimethyl gallium entity. The relative stability of the trimer was 14.85 kJ/mol lower compared to the dimer. The dimethyl substituted gallium hydroxide trimer has not been isolated as a pure compound, but as a hydrogen bonded adduct [23]. X-ray crystallography of this adduct has shown that the dimethyl derivative is in a skew boat conformation. On the other hand the trimeric *t*-Bu derivative is forced into a conformation with a planar  $\text{Ga}_3\text{O}_3$  ring [18,19]. The crystal structure of  $[(t\text{-Bu})_2\text{Ga}(\mu\text{-OH})]_3$  also reveals that oxygen possesses a trigonal, planar geometry [19]. This is also nearly the case in the much less hindered DFT geometry of  $[\text{Me}_2\text{Ga}(\mu\text{-OH})]_3$ .

The most stable oligomer of the series is the tetrameric dimethylgallium hydroxide according to the computations. It was found by the DFT calculations to be of  $\text{C}_{2h}$  symmetry, with a  $\text{C}_2$  axis intersecting two gallium atoms, and with an orthogonal symmetry plane. In this oligomer the geometry around oxygen was trigonal planar with co-planar Ga-OH-Ga units forming a puckered 8-membered ring. Compared to the DFT geometry, the structure of the free tetramer in the crystal was also found to have inversion symmetry, but without a symmetry plane and a twofold axis [14]. The bond lengths and angles found in the crystal structure are very similar to those shown in Table 2 for the DFT geometry. The important Ga-O-Ga and O-Ga-O angles were 98.6°-98.9° and 133.0°-133.2° with a standard deviation of 1.2°-2° in the crystal structure, were found to be 99.6°-99.7° and 134.8° respectively in the DFT structure. The DFT results are thus within the experimental uncertainty of the crystal structure determination.



### Force field computations.

The widely different geometries of the oligomers are difficult to reproduce exactly with a simple force field like the one chosen here, MOME97, and the present results are therefore likely to be further refined in the future. However, while DFT and other *ab initio* methods still are time consuming and demand a certain training, simple force field computations are widely used and they can easily cope with a number of *t*-butyl groups and other bulky additions to an inorganic core. Results are shown in Table 3.

**Table 3.** Comparisons between results from force field calculations and experimental data. In case more than one observable is measured only an average value is shown.

Species	Ref.	Ga-C /Å	Ga-O /Å	O-Ga- C/1°	O-Ga- O/1°	Ga-O- Ga/1°	C-Ga- C/1°	Strain / kJ per Ga
(Me <sub>2</sub> GaOH) <sub>2</sub>	* exp	1.99	1.98	109	78	102	128	
	calc	1.97	1.95	114	77	103	115	49
(Me <sub>2</sub> GaOH) <sub>3</sub>	skewed boat [23] exp	1.95	1.94	107	97	128	125	
	skewed boat calc.	1.97	1.94	109	109	124	111	33.7
	boat calc.	1.97	1.94	111	104	122	111	32.5
	chair calc	1.97	1.94	111	102	122	110	32.0
(Me <sub>2</sub> GaOH) <sub>4</sub>	[13, 14] exp	1.98	1.94	107	101	133	125	
	calc	1.97	1.94	109	101	125	109	29.9
(2-pr <sub>2</sub> GaOH) <sub>2</sub>	[26] exp	1.99	1.94	110	81	99	123	
	calc	1.99	1.97	112	77	103	119	291/3
(Bu <sub>2</sub> GaOH) <sub>2</sub>	** exp	1.96	1.95	112	80	100	117	
	calc.	1.99	1.95	114	75	105	115	65
(Bu <sub>2</sub> GaOH) <sub>3</sub>	[14] exp	1.99	1.96	108	97	143	123	
	calc.	1.99	1.94	108	114	126	116	41
(Bu <sub>2</sub> GaOH) <sub>4</sub>	calc							50

\*) DFT computations in this communication; \*\*) This work

One noticeable choice of force field parameter is the low value for the bending force constant for the angle Ga-O-Ga of only 0.050 mdyn rad<sup>-1</sup>. It is satisfying to see that a high degree of flexibility

of the Ga-O-Ga bond angle recently has been noted to explain preparative conditions.<sup>31</sup> Another unusual aspect is the presence of the planar four-membered ring with a small O-Ga-O angle of 78° and accordingly a Ga-O-Ga angle of 102°. These aspects were modeled by using a Ga-Ga non-bonded interaction and allowing for 1,3 interactions to achieve a Ga-Ga repulsion important for ring geometries. The structures of [(CH<sub>3</sub>)<sub>2</sub>GaOH]<sub>2</sub>, [(CH<sub>3</sub>)<sub>2</sub>GaOH]<sub>3</sub>, and [(CH<sub>3</sub>)<sub>2</sub>GaOH]<sub>4</sub> have been relatively well reproduced by computations using MOMECC97 and the few extra parameters concerning gallium(III), see experimental section with Table 5.

The calculated strain energies for [Me<sub>2</sub>Ga(μ-OH)]<sub>n</sub> are 50, 34 and 31 kJ/mol for n = 2, 3 and 4, respectively. The force field calculation thus suggests that the tetramer is the most stable isomer in the series [Me<sub>2</sub>Ga(μ-OH)]<sub>n</sub> and the relative tendencies are in agreement with the DFT results. The important extension to the *t*-butyl analogs gave strain energies per gallium found to be 64 kJ/mol in [(*t*-Bu)<sub>2</sub>Ga(μ-OH)]<sub>2</sub> and only 41 kJ/mol in [(*t*-Bu)<sub>2</sub>Ga(μ-OH)]<sub>3</sub>, which accordingly must be considered the most stable of the two oligomers. The tetramer has a higher calculated strain energy per gallium of 49 kJ/mol in this case.

### 3. Conclusion

The dimer of di-*t*-butylgalliumhydroxide is found in the crystal formed by co-crystallizing di-*t*-butylgalliumhydroxide with the macrocyclic compound, 1,12-diaza-3,4:9,10-dibenzo-5,8-dioxo-cyclo-pentadecane, **I**. It is shown by DFT and force field computations that the dimer should be less stable than the trimer and it is therefore concluded that when co-crystallizing with the macrocyclic compound **I**, the dimer of di-*t*-butylgalliumhydroxide is stabilized due to the formation of a hydrogen bonded adduct. The calculated stabilization due to each hydrogen bond need only to be of the order of 10 kJ/mol and this is considered non-problematic.

It is assumed that geometrical isomers should be formed in amounts according to energy differences between isomers like those discussed here with different nuclearity. This assumption is considered reasonable when labile coordination compounds are considered. Thus in solution we should expect the dimer to be much less abundant than the trimer and the tetramer. Gas-phase density functional theoretical calculations on the dimethyl substituted gallium hydroxide oligomers confirm that the monomer and dimer are much less stable than the trimeric and tetrameric forms. The dialkyl gallium hydroxide oligomers present an interesting case where an increase in steric crowding leads to a stabilization of the smaller oligomers, despite the increase in strain energy associated with smaller ring size.

## 4. Experimental Section

### General

All manipulations during synthesis were performed under dry nitrogen atmosphere. Benzene and toluene were dried by distillation over lithium aluminum hydride under nitrogen prior to use. The macrocycle 1,12-diaza-3,4:9,10-dibenzo-5,8-dioxocyclo-pentadecane, OenNtn, was synthesized according to the literature [32]. Gallium(III)chloride and *tert*-butyllithium were obtained from Fluka, <sup>1</sup>H NMR spectra were obtained on a Bruker AM 250 spectrometer using CDCl<sub>3</sub> solutions. Chemical shifts are reported relative to internal TMS standard. Melting points are here reported uncorrected.

### Preparation of (t-Bu)<sub>3</sub>Ga

Tri-*t*-butylgallium was prepared using a modified literature preparation [33]. Freshly sublimed gallium chloride (0.8 g, 4.54 mmol) was dissolved in 15 ml benzene. *t*-butyl lithium (8 ml of 1.5 M pentane solution, 13.62 mmol) was added dropwise to the magnetically stirred GaCl<sub>3</sub> solution over a 10 min. period. White together with gray precipitate was observed during the addition. The mixture was heated to 70 °C for 15 hrs.; allowed to cool and filtered. A brown solution was obtained.

### Preparation of (t-Bu<sub>2</sub>GaOH)<sub>2</sub>·2 (OenNtn)

To the solution mentioned above was added OenNtn (0.71g, 2.27mmol). Gas evolution was observed immediately. The mixture was refluxed with stirring overnight, and solvent was removed by evacuation. The resulting solid was dissolved in warm benzene/toluene (1:1). Colorless blocks of crystals were obtained after 3 days. M.p. 145°C (decomposition); Yield 85% based on OenNtn. <sup>1</sup>H NMR: δ 0.8 (1H, s, OH), 1.10 (18H, s, *t*-Bu<sub>2</sub> Ga), 1.78 (2H, quin, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N), 1.30 (2H, br. NH), 1.65 (4H, t, NHCH<sub>2</sub>), 3.73 (4H, s, ArCH<sub>2</sub>), 4.35 (4H, s, OCH<sub>2</sub>), 6.9-7.35 (8H, m, Aromatic). The source of water necessary for the hydrolysis is unknown.

### Crystallography

X-ray diffraction data were collected with an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo K $\alpha$  radiation. The crystal was cooled to 122 K by an Oxford Cryosystems low temperature device during the experiment. The unit cell parameters were determined from a least squares refinement of the setting angles for 20 reflections with  $\theta$  in the range 17.8° – 20.4°. The intensity data were collected by operating the diffractometer in the  $\omega$ -2 $\theta$  scan mode, with  $\Delta\omega$  1.5° and the maximum scan time of 60 s. The intensities of five standard reflections monitored every 10000 sec. showed no systematic variations with exposure time, and the orientation of the crystal was checked

after every 600 reflections. Data reduction performed with the DREADD package included corrections for Lorentz and polarisation effects.<sup>34</sup> Determination of the structure by direct methods using SHELX [35,36] was attempted first in the centrosymmetric space group P-1. This attempt gave the positions of the two gallium atoms and it was also possible to localize the bridging hydroxo bridges and part of the *t*-butyl groups. However, attempts to localize the remaining atoms in form of an ordered structure turned out to be impossible. Structure determination was therefore attempted in the acentric space group P1, which revealed part of the structure. As the structure is close to being centrosymmetric the remaining of the atoms had to be introduced stepwise. After introduction of anisotropic displacement parameters for the non-hydrogen atoms a difference electron density map revealed the positions of the hydrogen atoms. Those attached to the carbon atoms were introduced and refined in idealized positions whereas the positions for the hydrogen atoms from amino and hydroxo groups were taken from the difference electron density and not included in the refinement. The pseudo symmetry made the refinement non-trivial. Different restraints were introduced in order to overcome these difficulties, the *t*-butyl groups by the SAME restraint and SADI restraint for the bond lengths of the four macrocycles and the Ga-ligand distances. Crystal data and the conditions for data collection are given in Table 4.

**Table 4.** Crystal data and structure refinement for the complex.

Formula	C <sub>27</sub> H <sub>43</sub> O <sub>3</sub> N <sub>2</sub> Ga	Crystal size/mm	0.15×0.14×0.14
Formula mass	513.37	$\theta_{\max}/^\circ$	26.97
Temperature/K	122(2)	Index range	0 ≤ h ≤ 17, -17
Wavelength/Å	0.71073		≤ k ≤ 17, -20 ≤
Crystal system	Triclinic		l ≤ 19
Space group	P1	Reflections collected	10618
a/Å	13.845(3)	Unique reflections	7266
b/Å	14.032(3)	Refinement on	F <sup>2</sup>
c/Å	16.406(7)	Data/restraints/parameters	10618 / 1856 /
$\alpha/^\circ$	99.20(2)		1143
$\beta/^\circ$	109.69(3)	Goodness-of-fit on F <sup>2</sup>	1.137
$\gamma/^\circ$	105.51(2)	Final R-indices:	R1 = 0.0506, I>2 $\sigma$ (I)
V/Å <sup>3</sup>	2779.5(15)		wR2 = 0.1068, all reflections
Z	4	$\Delta\rho$ max/eÅ <sup>-3</sup>	0.760 (located near Ga atoms)
D <sub>calc</sub> /Mg m <sup>-3</sup>	1.227	$\Delta\rho$ min/eÅ <sup>-3</sup>	-0.901
$\mu/\text{mm}^{-1}$	1.018		
F(000)	1096		

## 5. Theoretical calculations

### DFT calculations

All density functional theoretical calculations were performed as gas-phase calculations using Gaussian 98 Rev. A7 [37] on a dual processor Linux PC. Minimization of the total energy was achieved using the standard convergence criteria of Gaussian 98, through several geometry optimization and frequency calculations for each molecule. The final level of theory was the spin restricted B3LYP functional [38] with the TZV basis set [39] giving a total of 94, 188, 282, and 376 basis functions and 205, 410, 615, 820 primitive gaussians for the monomer, dimer, trimer, and tetrameric forms of dimethylgallium hydroxide respectively. No measures were taken to correct for possible basis set superposition errors. All species were charge neutral with singlet spin multiplicity. Initial coordinates were constructed using approximate bond lengths and angles adapted from crystal structures. Molecular symmetry was used with care. The initial coordinates were optimized without any type of symmetry restraints, and only when calculations converged to a structure possessing a particular symmetry element, were the coordinates adapted to allow the Gaussian 98 program to recognize the point group. The computed self-consistent field energies at the converged geometry were used as an estimate of their relative stabilities. Only the lowest energy conformers were considered in the DFT calculations.

**Table 5.** Gallium-related extra parameters used to simulate structures with MOMECC 97.

TYP	O	16.00	1	0	1	0	
TYP	GA	69.72	1	0	1	0	
STR	O	GA	3.00	1.90			
STR	GA	CT	4.00	1.97			
BEN	GA	O	GA	0.050	1.571		
BEN	GA	O	H	0.100	1.830		
BEN	O	GA	O	0.050	1.915		
BEN	O	GA	CT	0.100	1.915		
BEN	CT	GA	CT	0.100	1.915		
BEN	GA	CT	H	0.2	1.915		
NBD	GA	**	2.250	0.194			
TOR	**	GA	O	**	0.0010	6	0.524
TOR	**	CT	GA	**	0.0010	6	0.000

### Molecular modeling

MOMECC (version MOMECC97) [40] was used to model the gallium compounds with the extra parameters listed in Table 5.

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