

Di- μ -hydroxo-bis(diisopropylgallium)–1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (1/1)

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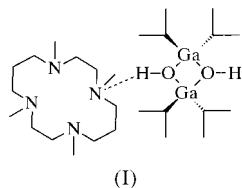
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The hydrolysis product $[\text{Ga}_2(\text{C}_3\text{H}_7)_4(\text{OH})_2] \cdot \text{C}_{14}\text{H}_{32}\text{N}_4$, derived from the tetrakis(triisopropylgallium)–1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (1/1) adduct, consists of a centrosymmetric $[\text{Pr}_2\text{Ga}(\mu\text{-OH})_2]$ unit hydrogen bonded through the hydroxyl group to a nitrogen on an adjacent centrosymmetric 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane molecule, resulting in the generation of a molecular chain through the crystal.

Comment

The product of controlled hydrolysis of gallium trialkyls depends on the steric bulk of the alkyl group and may result in tetramers, $[\text{Me}_2\text{Ga}(\mu_2\text{-OH})_4]$ (Smith & Hoard, 1959), trimers, $[\text{Bu}_2\text{Ga}(\mu_2\text{-OH})_3]$ (Naiini *et al.*, 1993; Atwood *et al.*, 1993), or dimers, $[\text{R}_2\text{Ga}(\mu\text{-OH})_2]$ [$\text{R} = \text{CH}(\text{SiMe}_3)_2$, mesityl, $\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2$] (Uhl *et al.*, 1996; Storre *et al.*, 1996; Coggin *et al.*, 1993). Increasing the steric congestion by substitution of the OH group by an alkoxide also results in a decrease in the degree of oligomerization, *e.g.* $[\text{Bu}_2\text{Ga}(\mu\text{-O}^t\text{Bu})_2]$ (Cleave *et al.*, 1994). This latter effect may apparently be mimicked by hydrogen bonding of the bridging hydroxyl species to an appropriate base, *e.g.* $[\text{Me}_3\text{Ga}(\mu\text{-OH})_3 \cdot 3\text{H}_2\text{O}]_2 \cdot 18\text{-crown-6}$ (Croucher *et al.*, 1999). This feature has allowed us to determine the molecular structure of $[\text{Pr}_2\text{Ga}(\mu\text{-OH})_2]$ as a hydrogen-bonded adduct, (I), of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane.



The molecule of (I) (Fig. 1) contains a centrosymmetric $\text{Ga}_2(\mu\text{-OH})_2$ four-membered ring with gallium-bonded isopropyl groups above and below the plane of the ring. The hydroxyl H atoms are located 0.38 (2) Å above/below this

plane, which subtends an angle of $\sim 152^\circ$ to the O–H vector.

The structure is analogous to other $[\text{R}_2\text{Ga}(\mu\text{-OH})_2]$ species and also to the chloride-substituted compounds $[\text{R}(\text{Cl})\text{Ga}(\mu\text{-OH})_2]$ [$\text{R} = 2,4,6\text{-}i\text{Pr}_3\text{Ph}$, $2,4,6\text{-}(\text{CF}_3)_3\text{Ph}$ or $(\text{Me}_3\text{Si})_3\text{Si}$] (Twamley & Power, 1999; Schluter *et al.*, 1994; Linti *et al.*, 1996).

The intra-annular Ga–Ga vector, 2.9425 (7) Å, is the shortest of the reported dialkyl derivatives, $[\text{R}_2\text{Ga}(\mu\text{-OH})_2]$ (2.970–3.064 Å), presumably due to reduced steric hindrance. Accordingly, the internal angle subtended at gallium, 81.04 (6)°, is larger than that found in the other six examples of this structural type (78.8–80.6°) and the corresponding angle at oxygen, 98.96 (6)°, is the smallest (99.1–102.1°). The Ga–O bond lengths, 1.9339 (12) and 1.9368 (12) Å, are compatible with the range of Ga–O bonds found in the other four-membered-ring species, 1.893–1.969 Å. However, the Ga–O bonds in the chloride-substituted derivatives, $[\text{R}(\text{Cl})\text{Ga}(\mu\text{-OH})_2]$, are generally shorter, which leads to shorter intra-annular Ga–Ga vectors (2.887–2.939 Å). The Ga–C bonds are some 0.03 Å shorter than the average found for adducts of $i\text{Pr}_3\text{Ga}$ (Coward *et al.*, 2000), where the bond length sequence Ga–Me < Ga–Et < Ga– $i\text{Pr}$ was demonstrated. However, they are comparable to those in other $\mu_2\text{-OH}$ gallium species, such as $[\text{Me}_2\text{Ga}(\mu_2\text{-OH})_4]$ (Smith & Hoard, 1959) and $[\text{Bu}_2\text{Ga}(\mu_2\text{-OH})_3]$ (Atwood *et al.*, 1993), although there are insufficient accurately determined data to confirm a similar sequence.

The four N atoms of the tetraazacyclotetradecane ring are crystallographically constrained to be coplanar. This plane subtends an angle of 82.71 (5)° to the plane of the Ga_2O_2 ring. Two independent ring configurations were found in the crystal structure of free 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, namely *RSSR trans-IV* and *RRSS trans-III* (Willey *et al.*, 1993; Kelly *et al.*, 1996). The tetraazacyclotetradecane ring in the gallium adduct adopts the higher

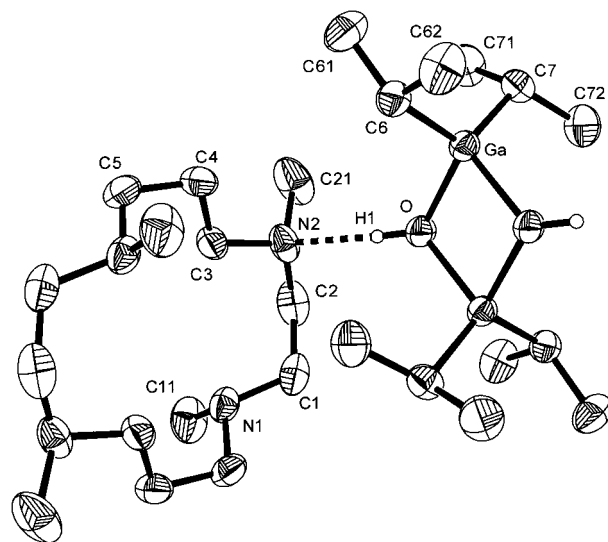


Figure 1

The molecular structure of (I) with displacement ellipsoids drawn at the 50% probability level.

energy *RRSS trans*-III configuration, which facilitates strong hydrogen bonding between N2 and the hydroxyl hydrogen, 2.03 (2) Å. The hydrogen bonds are approximately parallel to the *c* axis, resulting in a molecular chain running throughout the crystal. Apart from a possible intra-annular interaction between N1 and H3A (2.40 Å), there are no non-classical hydrogen bonds present.

Experimental

The 4:1 adduct of triisopropylgallium and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Coward *et al.*, 2000) was dissolved in dry toluene and left to crystallize at 243 K. After one week, there was evident decomposition, presumably due to hydrolysis. A few well shaped crystals present in the mixture were isolated and dried in a stream of dinitrogen.

Crystal data

[Ga ₂ (C ₃ H ₇) ₄ (OH) ₂]-C ₁₄ H ₃₂ N ₄	Z = 1
<i>M_r</i> = 602.24	<i>D_x</i> = 1.209 Mg m ⁻³
Triclinic, P $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 8.5877 (7) Å	Cell parameters from 32 reflections
<i>b</i> = 9.7161 (17) Å	θ = 5.44–15.04°
<i>c</i> = 11.1425 (10) Å	μ = 1.654 mm ⁻¹
α = 113.138 (8)°	<i>T</i> = 223 (2) K
β = 97.516 (4)°	Block, colourless
γ = 98.551 (7)°	0.45 × 0.30 × 0.25 mm
<i>V</i> = 826.92 (18) Å ³	

Data collection

Siemens <i>P4</i> diffractometer	<i>R</i> _{int} = 0.018
Profile fitting of $\theta/2\theta$ scans	θ_{\max} = 27.5°
Absorption correction: ψ scan	<i>h</i> = -1 → 11
(<i>XPREP</i> in <i>SHELXTL-Plus</i> ;	<i>k</i> = -11 → 11
Siemens, 1995)	<i>l</i> = -14 → 14
<i>T</i> _{min} = 0.568, <i>T</i> _{max} = 0.661	3 standard reflections
4385 measured reflections	every 97 reflections
3645 independent reflections	intensity decay: 5%
3277 reflections with <i>I</i> > 2σ(<i>I</i>)	

Refinement

Refinement on <i>F</i> ²	H atoms treated by a mixture of independent and constrained refinement
<i>R</i> (<i>F</i>) = 0.026	(Δ/σ) _{max} = 0.001
<i>wR</i> (<i>F</i> ²) = 0.065	$\Delta\rho_{\max}$ = 0.34 e Å ⁻³
<i>S</i> = 1.036	$\Delta\rho_{\min}$ = -0.22 e Å ⁻³
3645 reflections	
164 parameters	

The H atoms were placed in calculated positions and allowed to ride except for the hydroxyl hydrogen which was identified from a difference map and allowed to refine freely.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Siemens, 1995); software used to prepare material for publication: *SHELXL97*.

Table 1

Selected geometric parameters (Å, °).

Ga—O ⁱ	1.9339 (12)	Ga—C6	1.9872 (18)
Ga—O	1.9368 (12)	Ga—Ga ⁱ	2.9425 (7)
Ga—C7	1.9853 (18)		
O ⁱ —Ga—O	81.04 (6)	O—Ga—C6	112.91 (7)
O ⁱ —Ga—C7	112.84 (7)	C7—Ga—C6	123.30 (8)
O—Ga—C7	109.58 (7)	Ga ⁱ —O—Ga	98.96 (6)
O ⁱ —Ga—C6	109.36 (7)		

Symmetry code: (i) 1 - *x*, 1 - *y*, 1 - *z*.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O—H1...N2	0.80 (2)	2.03 (2)	2.8119 (19)	167 (2)

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1426). Services for accessing these data are described at the back of the journal.

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