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Organogallium chemistry of macrocyclic amines. Synthesis and molecular structure of $[\text{Ga}(\text{CH}_3)_3]_4[(\text{CH}_3)_4[14]\text{aneN}_4]$ and $[\text{Ga}(\text{CH}_3)]_2[14]\text{aneN}_4[\text{Ga}(\text{CH}_3)_3]_2$

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Abstract

Reaction of trimethylgallium with the tetradentate macrocyclic amine $[(\text{CH}_3)_4[14]\text{aneN}_4]$ in toluene affords the crystalline adduct product $[\text{Ga}(\text{CH}_3)_3]_4[(\text{CH}_3)_4[14]\text{aneN}_4]$, I. I crystallizes in the orthorhombic space group $Pbca$ (No. 61) with unit cell parameters $a = 14.002(2)$, $b = 18.542(3)$, $c = 14.477(3)$ Å, $V = 3758.6$ Å³, and $D_{\text{calc}} = 1.26$ g cm⁻³ for $Z = 4$. Full-matrix least-squares refinement based upon 2222 observed reflections converged at $R = 0.039$ ($R_w = 0.060$). Due to the four trimethylgallium units the macrocycle in I has been forced to assume an exodentate conformation. I resides about a crystallographic center of symmetry with independent Ga–N bond distances of 2.182(4) and 2.202(4) Å. The crystalline product $[\text{Ga}(\text{CH}_3)]_2[14]\text{aneN}_4[\text{Ga}(\text{CH}_3)_3]_2$, II, isolated from reaction of trimethylgallium with $[14]\text{aneN}_4$ in toluene, crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with unit cell parameters $a = 8.016(4)$, $b = 9.437(3)$, $c = 9.669(3)$ Å, $\alpha = 75.53(3)$, $\beta = 67.80(4)$, $\gamma = 73.26(4)^\circ$, $V = 640.2$ Å³, and $D_{\text{calc}} = 1.54$ g cm⁻³ for $Z = 1$. Full-matrix least-squares refinement based upon 1694 observed reflections converged at $R = 0.042$ ($R_w = 0.059$). II resides about a crystallographic center of symmetry with a planar Ga_2N_2 four-membered ring occupying the central cavity of the macrocycle. The Ga_2N_2 ring has a mean Ga–N bond distance of 2.009(6) Å. The Ga–N–Ga bond angle in the Ga_2N_2 ring is $90.2(2)^\circ$ while the N–Ga–N bond angle is $89.8(2)^\circ$. The Ga···Ga contact of 2.847(1) Å does not suggest significant metal–metal interaction. The Ga–N distances in I and II are among the longest reported.

Introduction

Organogallium chemistry is presently experiencing considerable activity. Whereas the utility of gallium in the diagnosis of disease has attracted attention in biological and medicinal fields [1–3], current interest in the inorganic and organometallic chemistry of gallium may principally be traced to the use of gallium in the production of semiconductor materials [4–10]. Although various III–V compounds have recently been under intense investigation, the literature reveals a relative paucity of studies concerning the interaction of organogallium species with Group V-based multidentate ligands. While the capacity of macrocyclic amines (i.e., nitrogen-based crown ethers) such as those shown in Fig. 1 to form stable complexes with transition metal ions has long been well recognized [11–17], the organogallium chemistry of these ligands has largely been ignored. Herein, we report the synthesis and molecular structure of $[\text{Ga}(\text{CH}_3)_3]_4[(\text{CH}_3)_4[14]\text{-aneN}_4]$, I, and $[\text{Ga}(\text{CH}_3)_2[14]\text{-aneN}_4][\text{Ga}(\text{CH}_3)_3]_2$, II. The Lewis acid adduct product I results from reaction of trimethylgallium with the macrocyclic tertiary amine $[(\text{CH}_3)_4[14]\text{aneN}_4]$, *N*-tetramethylcyclam, in toluene. II, isolated from reaction of trimethylgallium with $[14]\text{aneN}_4$ (cyclam) in toluene, contains a Ga_2N_2 four-membered ring resulting from cleavage of N–H fragments of the amine and Ga–C bonds of trimethylgallium units. This study represents the initial report regarding the organogallium chemistry of macrocyclic tetradentate amines.

Experimental

General comments

Standard Schlenk techniques were employed in conjunction with an inert atmosphere dry box (Vacuum Atmospheres HE-43 Dri-Lab). Toluene was distilled over sodium–benzophenone under an atmosphere of argon prior to use. Trimethylgallium, generously donated by Ethyl Corp. was used as received. $[(\text{CH}_3)_4[14]\text{aneN}_4]$, purchased from Aldrich Chemical Co., was used as received. The macrocyclic tetradentate secondary amine $[14]\text{aneN}_4$, was prepared in our laboratory by the Ni-template method described by Barefield et al. [18]. ^1H NMR spectra were recorded on an IBM 200 MHz NMR spectrometer. IR spectra were recorded on a Nicolet DX5 FT-IR spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

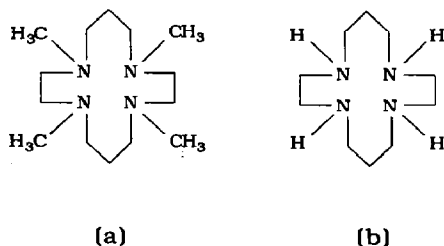


Fig. 1. Macrocyclic tetradentate amines: (a) $[(\text{CH}_3)_4[14]\text{aneN}_4]$; (b) $[14]\text{aneN}_4$.

Synthesis of [Ga(CH₃)₃]₄[(CH₃)₄[14]aneN₄], I

A reaction vessel was charged with [(CH₃)₄[14]aneN₄] (0.95 mmol) and taken into the dry box. Inside the dry box, toluene (30 ml) and trimethylgallium (8.0 mmol) were added to the reaction vessel. The reaction tube was removed from the dry box and heated (130 °C) in an oil bath for 6 hours. A multitude of colorless, rectangular, air-sensitive, X-ray quality crystals of I began to form in the reaction vessel while still in the oil bath. I was obtained in quantitative yield (based on [(CH₃)₄[14]aneN₄]). M.p. = 195–198 °C. ¹H NMR (CDCl₃): 2.63 (bs, 16H, NCH₂CH₂CH₂N, NCH₂CH₂N), 2.18 (s, 12H, NCH₃), 1.85 (p, 4H, NCH₂CH₂CH₂N), -0.54 (s, 36H, Ga(CH₃)₃). Anal. Found: C, 43.65; H, 9.57. C₂₆H₆₈Ga₄N₄ calc: C, 43.65; H, 9.58%. Infrared spectrum (cm⁻¹, nujol); 4321 (s), 3600 (w), 589 (m), 530 (m).

Synthesis of [Ga(CH₃)₃]₂[14]aneN₄[Ga(CH₃)₃]₂, II

The macrocyclic amine [14]aneN₄ (1.25 mmol) was placed in a reaction vessel and taken into the dry box where toluene (30 ml) and trimethylgallium (5 mmol) were added. The reaction vessel was removed from the dry box and heated (130 °C) in an oil bath for 24 hours. Upon cooling to 70 °C a multitude of colorless, square, air-sensitive, X-ray quality crystals of II resulted in quantitative yield (based on [14]aneN₄). M.p. 250 °C (dec.) ¹H NMR (CDCl₃): δ 3.0 (cm, 16H, NCH₂CH₂CH₂N, NCH₂CH₂N), 1.59 (p, 4H, NCH₂CH₂CH₂N), 0.19 (s, 6H, Ga(CH₃)), -0.58 (s, 18H, Ga(CH₃)₃). Anal. Found: C, 36.24; H, 7.45. C₁₈H₄₄Ga₄N₄ calc: C, 36.26; H, 7.44%. Infrared spectrum (cm⁻¹, nujol): 4321 (s), 3607 (w), 531 (w), 482 (w).

X-Ray structure solution and refinement

Single crystals of I and II were mounted in thin-walled glass capillaries under an atmosphere of argon. X-Ray intensity data for both compounds were collected on an Enraf–Nonius CAD-4 diffractometer by the ω-2θ scan technique with Mo-Kα radiation (λ = 0.71073 Å). Calculations for both compounds were performed using the SHELX [19] system of computer programs.

Final lattice parameters for I as determined from a least-squares refinement of ((sin θ)/λ)² values for 25 reflections (θ > 20°) led to an orthorhombic cell of space group *Pbca* (No. 61) with unit cell parameters *a* = 14.002(2), *b* = 18.542(3), *c* = 14.477(3) Å, *V* = 3758.6 Å³, and *D*_{calc} = 1.26 g cm⁻³ for *Z* = 4. Least-squares refinement with isotropic thermal parameters led to *R* = 0.107. The geometrically constrained hydrogen atoms were placed in calculated positions (*d*(C–H) = 0.95 Å) with fixed thermal parameters (*B* = 5.5 Å²). The methyl hydrogen atoms were included as a rigid group with fixed thermal parameters. Refinement of nonhydrogen atoms with anisotropic temperature factors for I converged at *R* = 0.039 (*R*_w = 0.060). The final difference map revealed no feature greater than 0.3e⁻/Å³. Relevant crystallographic data are given in Table 1. Final fractional atomic coordinates for I are given in Table 2 while bond distances and angles for I are given in Table 3.

Final lattice parameters for II as determined from a least-squares refinement of ((sin θ)/λ)² values for 25 reflections (θ > 19°) led to a triclinic cell of space group *P1* (No. 2) with unit cell parameters *a* = 8.016(4), *b* = 9.437(3), *c* = 9.669(3) Å, α = 75.53(3), β = 67.80(4), γ = 73.26(4)°, *V* = 640.2 Å³, and *D*_{calc} = 1.54 g cm⁻³ for

Table 1

Crystal and data collection parameters for [Ga(CH₃)₃]₄[(CH₃)₄[14]aneN₄], I and [Ga(CH₃)₂][14]aneN₄ [Ga(CH₃)₃]₂, II

	I	II
Empirical formula	C ₂₆ H ₆₈ Ga ₄ N ₄	C ₁₈ H ₄₄ Ga ₄ N ₄
Color; habit	Colorless/parallelepiped	
Size, (mm)	0.50 × 0.60 × 0.50	0.25 × 0.28 × 0.43
Space group	orthorhombic, <i>Pbca</i>	triclinic, <i>P</i> $\bar{1}$
Unit cell dimens		
<i>a</i> , Å	14.002(2)	8.016(4)
<i>b</i> , Å	18.542(3)	9.437(3)
<i>c</i> , Å	14.477(3)	9.669(3)
α, deg		75.53(3)
β, deg		67.80(4)
γ, deg		73.26(4)
<i>V</i> , Å ³	3758.6	640.2
Molecules/cell	4	1
Molecular Weight	715.74	595.47
<i>D</i> _{calc} , g/cm ³	1.26	1.54
Diffractionmeter	Enraf-Nonius CAD-4/ω-2θ	
Radiation	Mo-Kα (λ = 0.71073 Å)	
Temperature, °C	22	
2θ range, deg	2.0 < 2θ < 50.0	
Reflections collected	3730	2251
Reflections obsd	2222	1694
<i>GOF</i>	0.47	1.28
<i>R</i>	0.039	0.042
<i>R</i> _w	0.060	0.059

Table 2

Final fractional coordinates for [Ga(CH₃)₃]₄[(CH₃)₄[14]aneN₄], I

Atoms	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (eq) ^a
Ga(1)	0.85441(3)	0.50974(3)	-0.28982(3)	2.63
Ga(2)	0.98913(4)	0.76319(3)	-0.08332(4)	3.28
N(1)	0.8344(2)	0.5330(2)	-0.1433(2)	2.17
N(2)	0.9671(3)	0.6709(2)	0.0101(2)	2.38
C(1)	0.9041(3)	0.5908(2)	-0.1166(3)	2.03
C(2)	0.8889(3)	0.6225(2)	-0.0217(3)	2.42
C(3)	1.0596(3)	0.6325(2)	0.0205(3)	2.69
C(4)	0.9383(3)	0.4301(3)	-0.0874(3)	2.86
C(5)	0.8420(3)	0.4676(2)	-0.0841(3)	2.49
C(6)	0.7350(3)	0.5605(3)	-0.1346(4)	3.17
C(7)	0.9366(4)	0.7021(3)	0.1000(3)	3.12
C(8)	0.9930(4)	0.4958(4)	-0.3069(5)	4.11
C(9)	0.7704(4)	0.4254(3)	-0.3038(4)	4.34
C(10)	0.8066(5)	0.5984(4)	-0.3477(4)	5.06
C(11)	1.0633(5)	0.8284(3)	-0.0034(5)	5.22
C(12)	1.0641(5)	0.7245(4)	-0.1873(4)	4.65
C(13)	0.8553(4)	0.7918(4)	-0.1102(6)	5.11

^a *B*(eq) = $\frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}]$.

Table 3

Bond distances (Å) and angles (deg) for [Ga(CH₃)₃]₄[(CH₃)₄[14]aneN₄], I

Ga(1)–N(1)	2.182(4)	Ga(1)–C(8)	1.973(6)
Ga(1)–C(9)	1.967(5)	Ga(1)–C(10)	1.963(5)
Ga(2)–N(2)	2.202(4)	Ga(2)–C(11)	1.970(6)
Ga(2)–C(12)	1.971(7)	Ga(2)–C(13)	1.986(6)
N(1)–C(1)	1.500(5)	N(1)–C(5)	1.489(6)
N(1)–C(6)	1.488(6)	N(2)–C(2)	1.489(5)
N(2)–C(3)	1.487(5)	N(2)–C(7)	1.487(6)
C(1)–C(2)	1.509(6)	C(3)–C(4a)	1.511(7)
C(4)–C(5)	1.518(6)		
N(1)–Ga(1)–C(8)	105.9(2)	N(1)–Ga(1)–C(9)	100.4(2)
C(8)–Ga(1)–C(9)	118.1(3)	N(1)–Ga(1)–C(10)	101.9(2)
C(8)–Ga(1)–C(10)	113.1(3)	C(9)–Ga(1)–C(10)	114.7(3)
N(2)–Ga(2)–C(11)	101.0(2)	N(2)–Ga(2)–C(12)	105.1(2)
C(11)–Ga(2)–C(12)	113.0(3)	N(2)–Ga(2)–C(13)	101.3(2)
C(11)–Ga(2)–C(13)	116.7(3)	C(12)–Ga(2)–C(13)	116.8(3)
Ga(1)–N(1)–C(1)	108.0(2)	Ga(1)–N(1)–C(5)	112.9(3)
C(1)–N(1)–C(5)	112.8(3)	Ga(1)–N(1)–C(6)	105.7(3)
C(1)–N(1)–C(6)	109.9(3)	C(5)–N(1)–C(6)	107.3(3)
Ga(2)–N(1)–C(2)	112.4(3)	Ga(2)–N(2)–C(3)	108.3(3)
C(2)–N(2)–C(3)	112.5(3)	Ga(2)–N(2)–C(7)	106.0(3)
C(2)–N(2)–C(7)	107.0(4)	C(3)–N(2)–C(7)	110.4(4)
N(1)–C(1)–C(2)	114.9(3)	N(2)–C(2)–C(1)	114.4(3)
N(2)–C(3)–C(4a)	116.7(4)	C(3a)–C(4)–C(5)	110.4(4)
N(1)–C(5)–C(4)	114.7(4)		

$Z = 1$. Least-squares with isotropic thermal parameters led to $R = 0.077$. The hydrogen atoms were treated in a fashion similar to that described for I. Refinement of nonhydrogen atoms with anisotropic temperature factors for II converged at $R = 0.042$ ($R_w = 0.059$). The final difference map revealed no feature greater than $0.7e^-/\text{Å}^3$. Crystallographic data for II is given in Table 1. Final fractional atomic

Table 4

Final fractional coordinates for [Ga(CH₃)₂]₂[14]aneN₄[Ga(CH₃)₃]₂, II

Atoms	x/a	y/b	z/c	$B(eq)^a$
Ga(1)	0.48409(9)	0.11583(8)	0.57734(8)	2.15
Ga(2)	0.1172(1)	0.30581(9)	0.81684(9)	2.96
N(1)	0.2193(7)	0.1923(6)	0.6273(6)	2.27
N(2)	0.5520(7)	0.0952(6)	0.3593(6)	2.29
C(1)	0.168(1)	0.3013(8)	0.5014(8)	2.90
C(2)	0.240(1)	0.2440(9)	0.3483(8)	3.26
C(3)	0.445(1)	0.2156(8)	0.2742(8)	2.91
C(4)	0.7512(9)	0.0796(8)	0.2667(8)	2.57
C(5)	0.8659(9)	−0.0600(8)	0.334(1)	3.23
C(6)	0.648(1)	0.191(1)	0.631(1)	3.75
C(7)	−0.155(1)	0.341(1)	0.868(1)	3.70
C(8)	0.221(1)	0.4901(9)	0.736(1)	4.48
C(9)	0.216(1)	0.116(1)	0.974(1)	4.62

^a $B(eq) = \frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}]$.

Table 5

Bond distances (Å) and angles (deg) for $[\text{Ga}(\text{CH}_3)]_2[14]\text{aneN}_4[\text{Ga}(\text{CH}_3)_3]_2$, II

Ga(1)–N(1)	1.943(5)	Ga(1)–N(2)	2.014(6)
Ga(1)–C(6)	1.933(7)	Ga(1)–N(2a)	2.003(6)
Ga(2)–N(1)	2.126(5)	Ga(2)–C(7)	1.993(8)
Ga(2)–C(8)	1.998(8)	Ga(2)–C(9)	1.994(8)
N(1)–C(1)	1.489(8)	N(1)–C(5a)	1.49(1)
N(2)–C(3)	1.485(8)	N(2)–C(4)	1.491(8)
C(1)–C(2)	1.55(1)	C(2)–C(3)	1.50(1)
C(4)–C(5)	1.53(1)		
N(1)–Ga(1)–N(2)	100.2(2)	N(1)–Ga(1)–C(6)	125.7(3)
N(2)–Ga(1)–C(6)	117.7(3)	N(1)–Ga(1)–N(2a)	90.7(2)
N(2)–Ga(1)–N(2a)	89.8(2)	C(6)–Ga(1)–N(2a)	124.4(3)
N(1)–Ga(2)–C(7)	102.6(3)	N(1)–Ga(2)–C(8)	103.7(3)
C(7)–Ga(2)–C(8)	115.0(4)	N(1)–Ga(2)–C(9)	105.7(3)
C(7)–Ga(2)–C(9)	114.5(4)	C(8)–Ga(2)–C(9)	113.5(4)
Ga(1)–N(1)–Ga(2)	110.0(2)	Ga(1)–N(1)–C(1)	112.8(4)
Ga(2)–N(1)–C(1)	107.0(4)	Ga(1)–N(1)–C(5a)	106.9(4)
Ga(2)–N(1)–C(5a)	109.7(4)	C(1)–N(1)–C(5a)	110.5(7)
Ga(1)–N(2)–C(3)	114.2(4)	Ga(1)–N(2)–C(4)	116.4(4)
C(3)–N(2)–C(4)	107.7(5)	Ga(1)–N(2)–Ga(1a)	90.2(2)
C(3)–N(2)–Ga(1a)	123.6(6)	C(4)–N(2)–Ga(1a)	104.1(4)
N(1)–C(1)–C(2)	115.5(6)	C(1)–C(2)–C(3)	114.8(6)
N(2)–C(3)–C(2)	115.3(6)	N(2)–C(4)–C(5)	110.2(5)
N(1a)–C(5)–C(4)	111.1(7)		

coordinates for II are given in Table 4 while bond distances and angles are given in Table 5.

Results and discussion

The reaction of organoaluminum species with monodentate amines is, arguably, the most celebrated reaction in organoaluminum chemistry. Although initial investigations were mainly concerned with the reaction of aluminum alkyls with monodentate amines [20,21], the field has recently progressed to include the organoaluminum chemistry of macrocyclic and multidentate amines [22–24]. These reactions, characterized by Al–R/N–H bond cleavage, results in unusual aluminum–nitrogen cage products with aluminum often in unusual coordination environments. Whereas the organogallium chemistry of monodentate amines is not as extensively developed as that of aluminum, studies concerning organogallium–macrocyclic amine chemistry are noteworthy by their absence. In an effort to address this area of organogallium chemistry we report the synthesis and molecular structure of $[\text{Ga}(\text{CH}_3)_3]_4[(\text{CH}_3)_4[14]\text{aneN}_4]$, I, and $[\text{Ga}(\text{CH}_3)]_2[14]\text{aneN}_4[\text{Ga}(\text{CH}_3)_3]_2$, II, isolated from reaction of trimethylgallium with the macrocyclic amines $[(\text{CH}_3)_4[14]\text{aneN}_4]$ and $[14]\text{aneN}_4$ (Fig. 1), respectively. I is an adduct product. While II contains two terminal trimethylgallium adducts, the core of the macrocycle contains a Ga_2N_2 ring resulting from cleavage of N–H and Ga–C bonds.

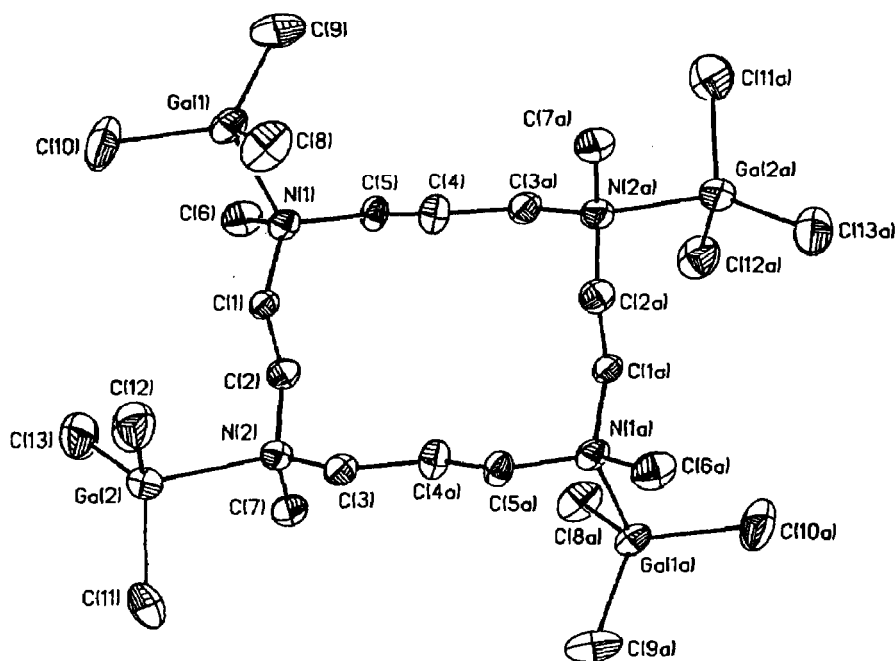
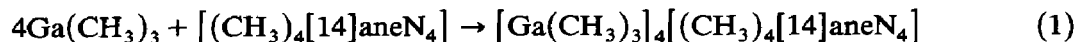


Fig. 2. A view of the $[\text{Ga}(\text{CH}_3)_3]_4[(\text{CH}_3)_4[14]\text{aneN}_4]$, I, molecule showing the atom labeling scheme. Thermal ellipsoids show 35% probability levels; hydrogen atoms have been omitted.

The X-ray crystal structure of I is given in Fig. 2. I was prepared by the reaction as described by eq. (1). I resides about a crystallographic center of symmetry with



the four nitrogen atoms of the amine being coplanar. Considering steric constraints about the tertiary nitrogen atoms, it is interesting that the adjacent gallium atoms, Ga(1) and Ga(2), reside on the same side of the N_4 -plane at displacements of 1.66 and 1.44 Å, respectively. The associated *N*-methyl carbon atoms, C(6) and C(7), reside on the opposite side of the N_4 -plane at displacements of 0.970 and 1.16 Å, respectively. The Ga–N bond distances are particularly worthy of note. As can be seen from Table 6, the independent G–N bond distances of 2.182(4) and 2.202(4) Å of I are among the longest Ga–N bond distances reported. The elongation of these Ga–N bond distances may be considered a consequence of the steric crowding associated with the tertiary nitrogen atoms of the macrocyclic amine.

Another point worthy of note is the conformation of $[(\text{CH}_3)_4[14]\text{aneN}_4]$ in I. The ability of $[(\text{CH}_3)_4[14]\text{aneN}_4]$ to form stable complexes with transition metal ions is well documented [15–17]. In all of these complexes the conformation of the macrocycle may be described as endodentate (the four nitrogen atoms of the amine directed towards the core of the macrocycle). The conformation of the macrocycle in I is clearly exodentate (the four nitrogen atoms directed away from the core of the macrocycle). The $[(\text{CH}_3)_4[14]\text{aneN}_4]$ macrocycle was also observed to be in the exodentate conformation in the aluminum analog of I [22]. As organoaluminum-crown ether complexes have been shown to serve as precursors to liquid clathrates [25] (liquid inclusion compounds), it is reasonable that I, in the presence of

Table 6

Comparisons of Ga–N bond distances (Å) in some organogallium compounds

Compound	Ga–N	Ref.
[(CH ₃) ₂ GaN ₂ C ₃ H ₃] ₂ ^a	1.985(9)	26
	1.995(9)	
	2.006(8)	
	2.002(9)	
[(CH ₃) ₂ GaN ₂ C ₅ H ₇] ₂ ^a	1.988(5)	27
	1.998(5)	
[(CH ₃) ₂ GaN=C(CH ₃) ₂] ₂ ^a	2.000(3)	28
	1.978(3)	
[(CH ₃) ₂ Ga(NCH ₃) ₂ CCH ₃] ₂ ^a	1.981(4)	29
	1.977(4)	
[(CH ₃) ₂ Ga(oxamide)] ₂ ^a	1.984(9)	30
	1.976(10)	
[(CH ₃) ₂ Ga][C ₁₂ H ₂₅ N ₂ O ₄][(CH ₃) ₃ Ga] ₂ ^b	2.164(5)	31
	2.171(6)	
[Ga(CH ₃) ₃] ₂ [C ₆ H ₁₂ N ₄] ^b	2.138(9)	32
[Ga(CH ₃) ₃] ₃ [C ₆ H ₁₂ N ₄] ^b	2.139(2)	32
[Ga(CH ₃) ₃] ₄ [(CH ₃) ₄ [14]aneN ₄] ^b	2.182(4)	this study
	2.202(4)	
[Ga(CH ₃) ₂][14]aneN ₄ [Ga(CH ₃) ₃] ₂ ^{a,b}	1.943(5)	this study
	2.126(5)	
	2.014(6)	
	2.003(6)	

^a Condensation product. ^b Adduct.

appropriate metal salts, could facilitate the preparation of organogallium based liquid clathrates.

Unlike [(CH₃)₄[14]aneN₄], [14]aneN₄ has acidic hydrogen atoms and thus is amenable to condensation reactions. The macrocyclic tetradentate secondary amine [14]aneN₄ reacts with trimethylgallium in toluene according to eq. 2 to afford [Ga(CH₃)₂][14]aneN₄[Ga(CH₃)₃]₂, II. The X-ray crystal structure of II is given in

$$4\text{Ga}(\text{CH}_3)_3 + [\text{14}]\text{aneN}_4 \rightarrow [\text{Ga}(\text{CH}_3)]_2[\text{14}]\text{aneN}_4[\text{Ga}(\text{CH}_3)_3]_2 + 4\text{CH}_4 \quad (2)$$

Fig. 3. Several points are worthy of note regarding structure and bonding in II. The molecule resides about a crystallographic center of symmetry. Moreover, the macrocycle in II has experienced severe distortion. There are two types of methylgallium moieties: two trimethylgallium fragments and two methylgallium fragments. Indeed, condensation occurred with only two of the four reacting trimethylgallium molecules as each of the two lost two methyl groups. The product subsequently underwent adduct formation with the two remaining trimethylgallium molecules. The methylgallium, Ga(1)–C(6), bond distance is 1.933(7) Å. The mean Ga–C bond distance in the trimethylgallium fragment is 1.995(8) Å. Perhaps the most notable feature of II is the four-membered Ga₂N₂ ring residing about the central cavity of the macrocycle. The Ga₂N₂ ring is planar and slightly asymmetric with independent Ga–N bond distances of 2.014(6) and 2.003(6) Å for Ga(1)–N(2) and Ga(1)–N(2a), respectively. The Ga(2)–N(1) adduct bond (2.126(5) Å) is considerably shorter than those found in I. This may be considered a consequence of the steric crowdedness about the tertiary nitrogen atoms of [(CH₃)₄[14]aneN₄] in I. Moreover, it is

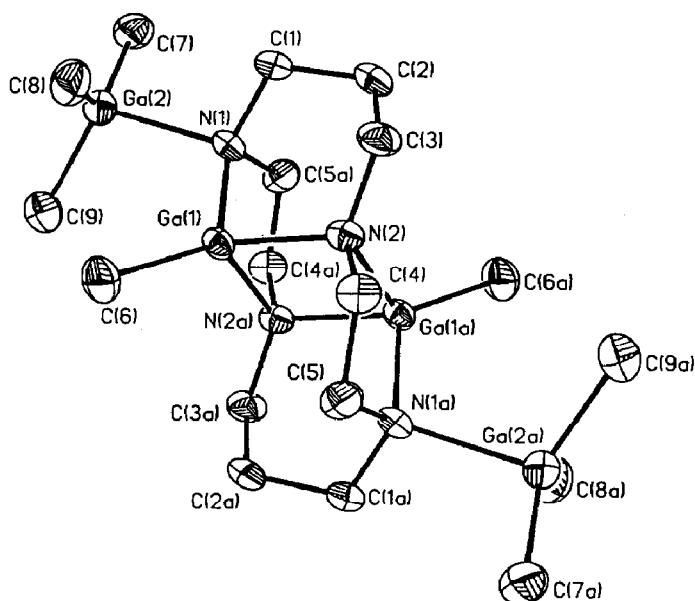


Fig. 3. A view of the $[\text{Ga}(\text{CH}_3)_2][14]\text{aneN}_4[\text{Ga}(\text{CH}_3)_3]_2$, II, molecule showing the atom labeling scheme. Thermal ellipsoids show 35% probability levels; hydrogen atoms have been omitted.

important to note that the $\text{Ga}(1)\text{--N}(1)$ “out of plane” bond distance (1.943(5) Å) is considerably shorter than the $\text{Ga}(1)\text{--N}(2)$ and $\text{Ga}(1)\text{--N}(2a)$ “in plane” bond distance (2.014(6) and 2.003(6) Å, respectively). Interestingly, the “in plane-out of plane” M--N ($\text{M} = \text{Ga}, \text{Al}$) bond distance relationship is found to be exactly opposite for the aluminum analog of II [23]. The Ga--N bond distances in II are compared with Ga--N distances reported for other organogallium compounds in Table 6. The $\text{Ga} \cdots \text{Ga}$ contact of 2.847(1) Å does not suggest significant metal–metal interaction. The Ga--N--Ga bond angle in the Ga_2N_2 ring is $90.2(2)^\circ$ while the N--Ga--N bond angle is $89.8(2)^\circ$. Unlike I, where the preparation of a gallium-based inclusion compound is favored, the presence of the Ga_2N_2 four-membered ring in II would greatly inhibit such reactivity.

The ability of trimethylgallium to form stable complexes with a macrocyclic tertiary amine coupled with the facile preparation of gallium–nitrogen condensation products will be used as a benchmark as we continue to explore the interactions of gallium alkyls with macrocyclic amines.

Supplementary material available. Tables of bond distances and angles, thermal parameters, and observed and calculated structure factors are available from the authors.

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