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Synthesis and Structural Characterization of the Novel Compounds from the Reactions of Trimethylaluminum or Trimethylgallium with N,O-Donor Crown Ethers

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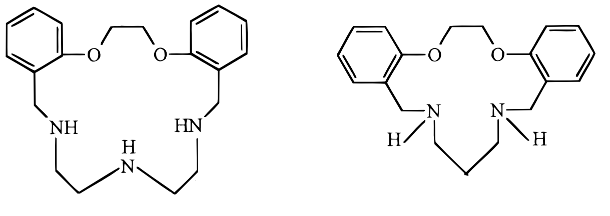
The reactions of two N/O mixed-donor crown ethers, 1,12,15-triaza-3,4:9,10-dibenzo-5,8-dioxacycloheptadecane (OenNdienH_4) and 1,12-diaza-3,4:9,10-dibenzo-5,8-dioxacyclopentadecane (OenNtnH_4) with MMe_3 (M = Al, Ga) are reported. OenNdienH_4 reacted with 3 equiv of $AlMe_3$ to form (AlMe)($AlMe_2$)(OenNdienH_4)($AlMe_3$) (**1**) which contains three different Me_nAl groups: AlMe, $AlMe_2$, $AlMe_3$. OenNtnH_4 reacted with 2 equiv of $AlMe_3$ to afford ($AlMe_2$)(OenNtnH_4)($AlMe_3$) (**2**) containing two chemically inequivalent aluminum centers. However, the reaction of OenNdienH_4 with $GaMe_3$ in 1:3 ratio resulted in (OenNdienH_4)$_2$($GaMe_2OH$)$_4$ (**3**). The (Me_2GaOH)$_4$ component contains an eight-membered Ga−O ring linked *via* four hydrogen bonds to two molecules of OenNdienH_4 which interacts from opposite sides of the Ga_4O_4 ring. The reaction of OenNtnH_4 with $GaMe_3$ in 1:2 ratio produced (OenNtnH_4)($GaMe_2OH$)$_3$ (**4**), a one-dimensional hydrogen bonded system which incorporates one OenNtnH_4 ligand and one nonplanar six-membered ring with alternating Ga and O atoms ($GaMe_2OH$)$_3$.

Introduction

In contrast to the reports of Group 13 derivatives of aza-crown and oxa-crown ethers, only relatively recently have studies been devoted to organoaluminum and organogallium derivatives of the N/O mixed-donor crown ethers. $[Ga(CH_3)_2][C_{12}H_{25}N_2O_4][Ga(CH_3)_3]_2$,[1] $[(EtAl_2)\cdot$diaza-18-crown-6$]^{2+}$ [2] and $Me_2Al[N18C6]AlMe_3$[3] have been reported. We have explored the reactions of $AlMe_3$ or $GaMe_3$ with 1,12,15-triaza-3,4:9,10-dibenzo-5,8-dioxacycloheptadecane (OenNdienH_4) and 1,12-diaza-3,4:9,10-dibenzo-5,8-dioxacyclopentadecane (OenNtnH_4) (Chart 1).

Aluminum trialkyls and gallium trialkyls often show similar reaction behavior toward the same kind of ligand,[4−7] but in the present case, the reactions of the macrocyclic ligands with Me_3Al or Me_3Ga resulted in two quite different types of products under the same conditions.

Chart 1. Structural Formulas of (a) OenNdienH_4 and (b) OenNtnH_4



(a) OenNdienH_4 **(b)** OenNtnH_4

Experimental Section

General Comments. All manipulations were performed in a HE-493 Dry-Train Drybox under nitrogen atmosphere. All solvents were dried by distillation from the sodium/benzophenone under nitrogen prior to use. The ligands OenNdienH_4[8] and OenNtnH_4[9] were synthesized according to literature methods. Trimethylaluminum and trimethylgallium were provided by Special Gas Institute of Nanjing University. IR spectra were recorded in Nujol mulls on a Nicolet 170SX FT-IR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained with a Bruker AM 500 spectrometer in C_6D_6 using $SiMe_4$ as internal reference. Mass spectra were obtained on a ZAB-HS spectrometer operating in the electron ionization mode at 70 eV. Elemental analyses were obtained on a Perkin-Elmer 240C analyzer.

Preparation of (AlMe)($AlMe_2$)(OenNdienH_4)($AlMe_3$) (1). OenNdienH_4 (0.51 g, 1.5 mmol) was suspended in 20 mL

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of toluene and stirred while a solution of trimethylaluminum (0.42 mL, 4.5 mmol) in 10 mL of toluene was added at room temperature. A homogeneous solution resulted gradually within 30 min, and then the solution was heated at 50 °C for 10 h. Concentration of the reaction mixture yielded colorless single crystals suitable for X-ray analysis. Yield: 0.67 g, 90%. ^{1}H NMR (500 MHz, C_6D_6): δ −0.39 (3H, s, AlCH_3); 0.15 (6H, s, Al$(CH_3)_2$); 0.29 (9H, s, Al$(CH_3)_3$); 2.48 (8H, m, NCH_2); 3.69 (4H, s, PhCH_2); 3.92 (4H, s, OCH_2); 6.49−7.13 (8H, m, PhH). Anal. Calcd for $C_{26}H_{42}Al_3N_3O_2$: C, 61.30; H, 12.11; N, 8.25. Found: C, 60.56; H, 11.60; N, 7.32.

Preparation of $(AlMe_2)(OenNtnH_4)(AlMe_3)$ (2). The same procedure was used in the reaction of trimethylaluminum (0.36 mL, 3.8 mmol) in 10 mL of toluene with OenNtnH$_4$ (0.61 g, 1.9 mmol) in 20 mL of toluene. Colorless single crystals suitable for X-ray analysis were obtained. Yield: 0.76 g, 92%. ^{1}H NMR (500 MHz, C_6D_6): δ −0.53 (6H, s, Al$(CH_3)_2$); −0.28 (9H, s, Al$(CH_3)_3$); 2.32−2.49 (6H, m, NCH_2); 3.25 (4H, m, PhCH_2); 4.53 (4H, s, OCH_2); 6.40−7.28 (8H, m, PhH). Anal. Calcd for $C_{24}H_{37}Al_2N_2O_2$: C, 65.60; H, 8.42; N, 6.38. Found: C, 64.85; H, 8.32; N, 5.96.

Preparation of $(OenNdienH_4)_2(GaMe_2OH)_4$ (3). The same procedure was used in the reaction of OenNdienH$_4$ (0.52 g, 1.47 mmol) in 20 mL of toluene with trimethylgallium (0.44 mL, 4.60 mmol) in 10 mL of tolune. The product was recrystallized from benzene, giving colorless X-ray-quality crystals. Yield: 1.03 g, 75% based on Ga. ^{1}H NMR (500 MHz, C_6D_6): δ −0.50 (24H, s, Ga$(CH_3)_2$); 2.46 (4H, s, NCH_2); 2.50 (4H, s, NCH_2); 3.67 (4H, s, PhCH_2); 4.35 (4H, s, OCH_2); 6.88−7.37 (8H, m, C_6H_4). $^{13}C\{^1H\}$ NMR (125.77 MHz, C_6D_6): δ −4.59 ($GaCH_3$); 48.68, 49.02 (NCH_2); 50.73 ($PhCH_2$); 67.05 (OCH_2); 110.91, 120.61, 128.31, 128.79, 130.99, 157.13 (C_6H_4). IR (cm^{-1}): 3622.0 (s, O−H); 3208.8 (m, N−H). Anal. Calcd for $C_{30}H_{47}Ga_2N_3O_4$: C, 55.13; H, 7.19; N, 7.35. Found: C, 54.93; H, 6.80; N, 7.11.

Preparation of $(OenNtnH_4)(GaMe_2OH)_3$ (4). The same procedure was used in the reaction of trimethylgallium (0.66 mL, 6.4 mmol) with OenNtnH$_4$ (1.03 g, 3.2 mmol) in 20 mL of toluene. A white crystalline solid was obtained which was recrystallized from benzene to give single crystals suitable for X-ray analysis. Yield: 1.12 g, 80% based on Ga.

^{1}H NMR (500 MHz, C_6D_6): δ −0.65 (18H, s, Ga$(CH_3)_2$); 1.49 (2H, t, CH_2); 2.50 (4H, t, NCH_2); 3.37 (2H, br, NH); 3.60(4H, s, PhCH_2); 4.36 (4H, s, OCH_2); 6.88−7.36 (8H, m, C_6H_4). ^{13}C-$\{^1H\}$ NMR (125.77 MHz, C_6D_6): δ −4.1 (Ga-CH_3); 26.6 (CH_2); 48.7, 47.4 ($PhCH_2$); 66.5 (OCH_2); 110−157 (C_6H_4). IR (cm^{-1}): 3622.0 (s, O−H); 3308.8 (m, N−H). Anal. Calcd for $C_{25}H_{45}Ga_3N_2O_5$: C, 45.31; H, 6.79; N, 4.22. Found: C, 44.88; H, 6.50; N, 3.96.

X-ray Structural Solution and Refinement. The single crystals were mounted and flame-sealed in Lindmann capillaries. Data were collected at 294 K on a Siemens P4 Four-circle diffractometer with monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation using $\omega/2\theta$ scan mode with a variable scan speed 5.0−50.0° min^{-1} in ω. The intensities adjusted accordingly and corrected for Lorentz-polarization effects during data reduction using XSCANS.[10] No absorption correction were applied. All the structures were solved by direct method and refined on F^2 by full-matrix least-squares method using SHELXTL version 5.0.[11] All the non-hydrogen atoms were refined anisotropically. H(1D) and H(2D) attached to N(1) and N(2), respectively, in complex **4** were located directly from the difference Fourier maps. All the other hydrogen atoms were placed in calculated positions (C−H, 0.96; N−H, 0.90 and O−H, 0.85 Å) assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they are attached (1.5 times for the O−H and methyl groups) and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure-factor calcuations. All computations were carried out on a PC-586 computer using the SHELXTL-PC Program Package.[11] Analytical expressions of neutral-atom scattering factors employed and anomalous dispersion corrections were incorporated.[12]

Results and Discussion

Synthesis and Characterization. Reactions of OenNdienH$_4$ and OenNtnH$_4$ with AlMe$_3$ in a 1:3 and 1:2 ratio resulted in the formation of $(AlMe)(AlMe_2)(OenNdienH_4)(AlMe_3)$ (**1**) and $(AlMe_2)(OenNtnH_4)(AlMe_3)$ (**2**), respectively, in nearly quantitative yield. Both **1** and **2** are extremely sensitive to air and moisture and are poorly soluble in benzene. Their ^{1}H NMR spectra were obtained using a very dilute C_6D_6 solutions.

The reaction of OenNdienH$_4$ and OenNtnH$_4$ with GaMe$_3$ in 1:3 and 1:2 ratio, respectively, under the same conditions produced $(OenNdienH_4)_2(GaMe_2OH)_4$ (**3**) and $(OenNtnH_4)(GaMe_2OH)_3$ (**4**). Compounds **3** and **4** are less sensitive but decompose slowly when exposed to air and moisture. Both are soluble in benzene.

In the ^{1}H NMR spectra of complexes **1**−**4**, the signals due to the methyl group attached to aluminum and gallium were singlets at −0.39, −0.53, −0.50, and −0.65 ppm, respectively. The respective singlets at −4.59 and −4.1 ppm in the $^{13}C\{^1H\}$ NMR spectra of compounds **3** and **4** were assigned to the Ga-Me carbon atoms.

Molecular ion peaks were not observed in the mass spectra of **1**−**4**. The mass spectra of **1** and **2** showed strong fragment ion peaks due to $[M - Me]^+$ and $[M - AlMe]^+$. In contrast, in the mass spectra of **3** and **4**, the most intense peaks were those associated with fragmentation of Me$_3$Ga and the ligands. The base peaks were $[Me_2Ga]^+$.

Dimethylgallium(III) hydroxide is a known compound.[13,14] The formation of **3** and **4** could have proceeded *via* the Lewis acid−base adducts followed by the hydrolysis of the latter by a traces of H_2O present in the reaction medium. Even at higher temperature (100 °C) the preparative reactions gave **3** and **4**, as indicated by ^{1}H NMR spectra.

Structure and Bonding. Thermal ellipsoid diagrams of complexes **1**−**4** are shown in Figures 1−4. Crystal data and structure refinement for complexes **1**−**4** are given in Table 1. Complex **1** belongs to the monoclinic system $C2/c$ with eight molecules in the unit cell. The molecule possesses one Al_2N_2 fragment which is nearly planar with mean deviation from best plane of 0.050 Å. The Al_2N_2 plane is slightly asymmetric with average Al(1)−N and Al(2)−N distances of 1.960 and 2.00 Å, respectively. Compared to Al_2N_2 fragments in $[(MeAl)_2[14]aneN_4][AlMe_3]_2$ which contains the N(1)−Al(1)−N(2) bond angle of 101.3(2)°, and Al(1)−N(1)−Al(a) of 89.9(2)°,[15] the Al_2N_2 units in complex **1** forms a

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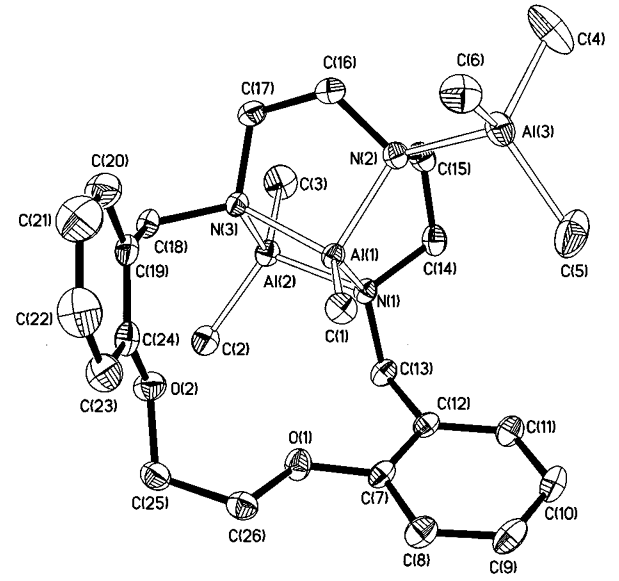

Figure 1. Molecular diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme of $(AlMe)(AlMe_2)(OenNdienH_4)(AlMe_3)$ (**1**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)−N(2), 1.928(3); Al(1)−N(1), 1.953(2); Al(2)−N(1), 1.990(2); Al(3)−N(2), 2.023(2); N(1)−Al(1)−N(3), 90.25(1), N(1)−Al(2)−N(3), 87.82(9); Al(1)−N(1)−Al(2), 91.20(9); Al(1)−N(3)−Al(2), 90.00(1).

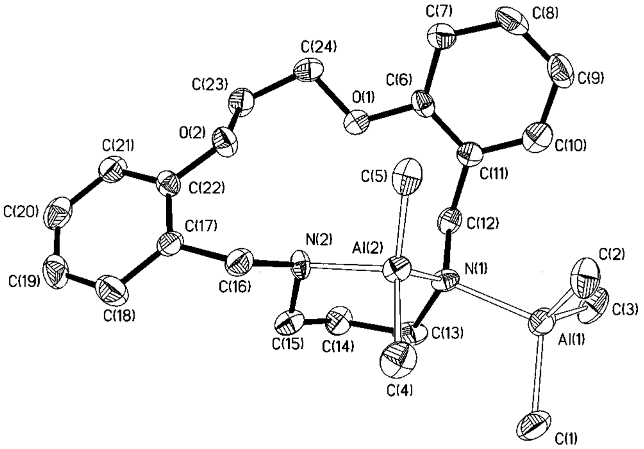

Figure 2. Molecular diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme of $(AlMe_2)(OenNtnH_4)(AlMe_3)$ (**2**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)−N(1), 2.060(5); Al(2)−N(2), 2.011(5); Al(2)−N(1), 1.945(5); N(1)−Al(2)−N(2), 96.9(2).

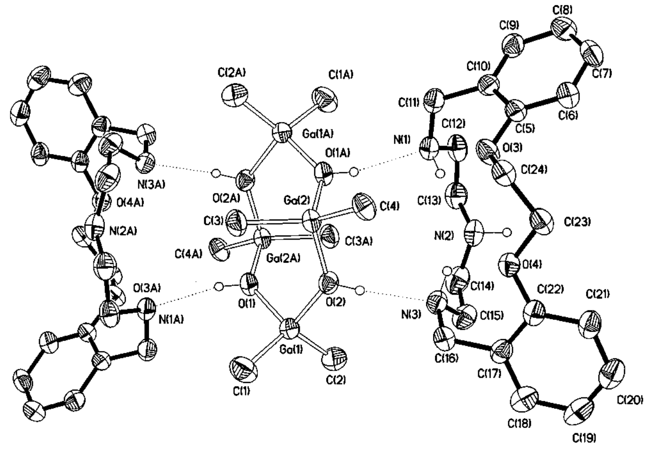

Figure 3. Molecular diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme of $(OenNdienH_4)_2(GaMe_2OH)_4$ (**3**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ga(1)−O(1), 1.910(4); Ga(2)−O(2), 1.914(4); O(2)−Ga(2)−O(1) no. 1, 102.1(2); Ga(1)−O(1)−Ga(2) no. 1, 133.5(2). Symmetry transformations used to generate equivalent atoms: no. 1 $-X + 1$, $-Y$, $-Z + 1$.

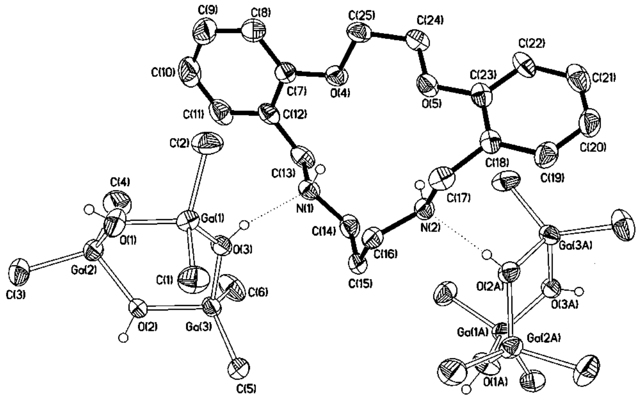

Figure 4. Molecular diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme of $(OenNtnH_4)(GaMe_2OH)_3$ (**4**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ga(1)−O(3), 1.892(3); Ga(1)−O(1), 1.927(4); O(3)−Ga(1)−O(1), 96.1(2); Ga(1)−O(1)−Ga(2), 129.1(2).

near-rectangle with an average angle of 90°. The Al···Al separation across the Al_2N_2 four-membered ring is 2.817(2) Å, which is similar to that observed in $[Al_4(\mu_3\text{-}8\text{-quinolylimide})_2(CH_3)_8]$ (2.788(5) Å).[16] There are three types of aluminum centers existing within the molecule. Al(1) has only one methyl, Al(2) has two methyl groups, while Al(3) possesses three methyl groups. The shortest Al−N bond is 1.928(3) Å for Al(1)−N(2) which is within normal covalent bonding with a slightly dative character. The Al(1)−N(1) (1.953(2) Å) and Al(1)−N(3) (1.968(2) Å) are slightly longer than the Al(1)−N(2) bond distance. The Al(2)−N(1) (1.990(2) Å) and Al(3)−N(2) (2.023(2) Å) are even longer and may have some dative character. These distances are similar to the mean Al−N bond distances of 2.02(3) Å in $[Al(CH_3)]_2[C_8H_{20}N_6][Al(CH_3)_2]_2$ containing a four-membered Al_2N_2 ring as a result of intermolecular condensation[17] and the dative bonds in $[AlEt_2]_2[C_{10}H_{22}N_4][AlEt_3]_2$ (2.073(4) and 2.025(4) Å).[18] The overall geometry of the nitrogen atoms is distorted tetrahedral. The average Al−C distance of 1.987(4) Å for Al(3) is slightly longer than that of 1.969(3) Å for Al(2) and 1.932(3) Å for Al(1).

Complex **2** crystallizes in the orthorhombic system $P2_12_12_1$ with four molecules in the unit cell. The geometry of Al(1) and Al(2) is distorted tetrahedral. The observed Al−C bond distances (average value of 1.977(6) Å) are similar to the reported values.[19] Complex **2**

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Table 1. Crystal Data and Structure Refinement for (AlMe)($AlMe_2$)($OenNdienH_4$)($AlMe_3$) (1), ($AlMe_2$)($OenNtnH_4$)($AlMe_3$) (2), ($OenNdienH_4$)$_2$($GaMe_2OH$)$_4$ (3), and ($OenNtnH_4$)($GaMe_2OH$)$_3$ (4)

	1	**2**	**3**	**4**
empirical formula	$C_{26}H_{42}Al_3N_3O_2$	$C_{24}H_{37}Al_2N_2O_2$	$C_{30}H_{47}Ga_2N_3O_4$	$C_{25}H_{45}Ga_3N_2O_5$
fw	509.57	439.52	653.15	662.79
temp, K	295(2)	293(2)	293(2)	291(2)
cryst system	monoclinic	orthorhombic	triclinic	monoclinic
space group	$C2/c$	$P2_12_12_1$	$P\bar{1}$	$P2_1/c$
a, Å	27.078(5)	9.847(4)	11.022(3)	8.9446(8)
b, Å	13.083(3)	16.123(3)	12.366(3)	16.126(6)
c, Å	19.80(2)	16.334(6)	14.562(3)	22.102(2)
α, deg	90	90	72.527(14)	90
β, deg	122.89(3)	90	74.14(2)	90.129(5)
γ, deg	90	90	66.494(12)	90
V, Å^3	5890(6)	2593.2(14)	1709.1(7)	3188.0(12)
D_{calcd}, g cm^{-3}	1.149	1.126	1.269	1.381
Z	8	4	2	4
abs coeff, mm^{-1}	0.154	0.133	1.611	2.549
$F(000)$	2192	948	684	1368
cryst dimens, mm	0.3 × 0.4 × 0.41	0.2 × 0.2 × 0.3	0.56 × 0.44 × 0.38	0.4 × 0.3 × 0.3
θ range for data colln, deg	1.79 to 24.99	1.77 to 24.99	1.84 to 25.00	1.84 to 22.50
no. of rflns colled	5306	2595	6340	5509
indepdt rflns	5190 ($R_{int} = 0.0195$)	2595 ($R_{int} = 0.0000$)	5997 ($R_{int} = 0.0403$)	4141 ($R_{int} = 0.0283$)
data/restraints/param	5185/0/307	2589/0/271	5997/9/352	4135/0/324
goodness-of-fit on F^2	1.017	0.946	1.017	1.063
final R indices^a [$I > 2\sigma(I)$]	$R1 = 0.0488$ $wR2 = 0.1229$	$R1 = 0.0621$ $wR2 = 0.0785$	$R1 = 0.0586$ $wR2 = 0.1334$	$R1 = 0.0379$ $wR2 = 0.0882$
R indices (all data)	$R1 = 0.0840$ $wR2 = 0.1468$	$R1 = 0.1900$ $wR2 = 0.1092$	$R1 = 0.1216$ $wR2 = 0.1707$	$R1 = 0.0660$ $wR2 = 0.1067$
D(r) and hole, e/Å^{-3}	0.243, −0.207	0.229, −0.222	0.532, −0.556	0.309, −0.487

[a] The R values presented are defined as $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, and $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$.

is an asymmetric molecule. The coordination environment between Al(1) and Al(2) are different. Al(1) possesses three methyl groups and bonds with N(1) in a dative fashion. The Al(1)−N(1) distance is 2.060(5) Å. Al(2) possesses two methyl groups and coordinates with two nitrogen atoms and forms a six-membered AlC_3N_2 ring in a chair conformation. The Al(2)−N(2) bond distance (2.011(5) Å) is similar to that of Al(1)−N(1), while Al(2)−N(1) (1.945(5) Å) is somewhat shorter than that of Al(1)−N(1).

Considering the great affinity of aluminum to oxygen, in addition to the fact that $OenNdienH_4$ and $OenNtnH_4$ possess both oxygen and nitrogen donor sites, it is worth noting that both $AlMe_3$ fragments in complexes **1** and **2** are coordinated to nitrogen rather than oxygen. This is in accord with the strong donor abilities of N atoms of the type R_2NM, where M is a polar metal or organometallic fragment. This coordination feature is significantly different from that observed for complex [($EtAl_2$)•diaza-18-crown-6] [$EtAlCl_3$]$_2$, in which both nitrogen and oxygen atoms are coordinated with Al atoms.[2] The conformation of $OenNdienH_4$ in complex **1** is endodentate. In contrast, studies by Atwood *et al.* demonstrated that organoaluminum moieties greatly distorted oxygen-based crown ethers and forced them to assume an unusual exodentate conformation upon adduct formation.[20,21]

Complex **3** crystallizes in the triclinic system $P\bar{1}$. The structure consists of one eight-membered Ga_4O_4 ring of alternating Ga and O atoms and two molecules of $OenNdienH_4$. There are two hydrogen bonds O-H···N involving two hydroxyl groups in Ga_4O_4 ring and two nitrogen atoms in the same molecule of ligand. The hydrogen bond distance for O(2A)−H(2D)···N(3A) (H(2D)···N(3A) 2.050 Å) is rather shorter than that for O(1A)−H(1D)···N(1) (H(1D)···N(1) 2.117 Å), and the corresponding hydrogen bond for the former (O(2A)−H(2D)···N(3A) 174.3°) is more linear than that for the latter (O(1A)−H(1D)···N(1) 156.8°). An X-ray investigation of uncomplexed ($GaMe_2OH$)$_4$ showed that the hydroxide is tetrameric in centrosymmetry and with two carbon and two oxygen atoms arranged tetrahedrally about gallium.[14] The tetramer ($GaMe_2OH$)$_4$ in complex **3** also adopts a centrosymmetric conformation. Comparing the structure of uncomplexed ($GaMe_2OH$)$_4$ with the corresponding part in complex **3**, we can observe that the average bond distances for Ga−O in the former is somewhat longer than that in the latter. This may be attributable to the O−H···N hydrogen bondings present in complex **3**, which strengthens the Ga−O bond and causes it to be shorter. The uncomplexed $OenNdienH_4$ macrocycle was shown to reside in an endodentate conformation, and the two aza hydrogen atoms were directed toward the center of the macrocyclic cavity as a consequence of both intramolecular and intermolecular hydrogen bonds.[22] However, $OenNdienH_4$ in complex **3** is in an exodentate conformation, and the two aza hydrogen atoms are exo to the macrocyclic ring. This conformation is stabilized by the hydrogen bonds.

Complex **4** crystallizes in the monoclinic system $P2_1/c$ with four molecules in the unit cell. The structure incorporates a hydrogen-bonding system involving one six-membered Ga_3O_3 ring with alternating Ga and O atoms and one molecule of $OenNtnH_4$. Two OH groups

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of the Ga_3O_3 ring acting as hydrogen donors are linked with two nitrogen atoms of the ligand acting as hydrogen acceptors, respectively, in an alternating fashion, with another OH group remaining free, thus resulting in a one-dimensional hydrogen bonding system. The hydrogen bond distances for O(2A)−H(2O)···N(2) (O(2A)···N(2) 2.820 Å, H(2O)···N(2) 1.992 Å) are similar to those for O(3)−H(3O)···N(1) (O(3)···N(1) 2.836 Å, H(3O)···N(1) 2.004 Å). The hydrogen bond angles for O(2A)−H(2O)···N(2) and O(3)−H(3O)···N(1) are 164.5° and 165.8°, respectively. The trimer $(GaMe_2OH)_3$ has a six-membered Ga_3O_3 ring in a skewed-boat conformation. In a comparison of complexes **3** and **4**, all bond distances in the trimer $(GaMe_2OH)_3$ are very close to the corresponding values in the tetramer $(GaMe_2OH)_4$. There is no obvious correlation between the Ga−O bond lengths and the ring sizes. The conformation of the ligand $OenNtnH_4$ is determined to be exodentate. However, the conformations of diaza-18-crown-6 in $[Ga(CH_3)_2][C_{12}H_{25}N_2O_4][Ga(CH_3)_2]$[1] and aza-18-crown-6 in $Me_2Al[N18C6]AlMe_3$[3] are found to be endodendate.

Both complexes **3** and **4** are stabilized by O−H···N hydrogen bonds between $(GaMe_2OH)_n$ and macrocycles. The degree of oligomerization of $(GaMe_2OH)_n$ seems dependent on number of nitrogen atoms and macrocyclic conformation. The geometry of binding interactions is differently affected by steric constraints and other features of molecular geometry. An alternative explanation of factors determining the ring size of $(GaMe_2OH)_n$ relates to hydrogen bonding patterns.

The reactions of $AlMe_3$ and $GaMe_3$ with $OenNdienH_4$ and $OenNtnH_4$, respectively, yielded quite different products. $AlMe_3$ underwent a condensation reaction involving the cleavage of Al−Me and N−H bonds resulting in condensation products, while $GaMe_3$ yielded novel hydrogen-bonded systems incorporating $(GaMe_2OH)_n$. Thus, the reaction between Me_3Ga and the macrocyclic ligands led to unexpected products rather than Ga analogues of compounds **1** and **2**. Subtle differences in the reactivity and structure of similar aluminum and gallium compounds have been reported previously. For example, in the case of heterobimetallic complex $[Al(CH_3)]_2[14]aneN_4[Ga(CH_3)_3]_2$, the two $AlMe_3$ units underwent condensations whereas $GaMe_3$ formed dative bonds.[23] In general, it is perhaps the main consequence of reactions of $AlMe_3$ and $GaMe_3$ with nitrogen-based crown ethers that aluminum adducts eliminate alkane at temperatures at which the gallium analogues are unaffected. The difference in reactivity between the Al and Ga compounds may relate to the greater Lewis acidity of $AlMe_3$.

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Supporting Information Available: Mass spectral data for **1**−**4**, unit cell diagrams for **3** and **4**, and tables of bond distances and angles, fractional atomic coordinates, and anisotropic and isotropic thermal parameters for **1**−**4** (22 pages). Ordering information is given on any current masthead page.

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