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# Isolation of Unusual Conformations of the [14]aneN$_4$ Aza Crown Ether: Syntheses and Molecular Structures of $[M(CH_3)_3]_2$[14]aneN$_4$ (M = Al, Ga) and the Group 13 Heterobimetallic Complex $[Al(CH_3)]_2$[14]aneN$_4$$[Ga(CH_3)_3]_2$

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Reaction of $M(CH_3)_3$ (M = Al, Ga) with the aza crown ether [14]aneN$_4$ affords crystalline complexes of the type $[M(CH_3)_3]_2$[14]aneN$_4$. The aluminum compound (I) crystallizes in the monoclinic space group $C2/c$ (No. 15) with unit cell parameters $a$ = 21.772 (4) Å, $b$ = 8.186 (2) Å, $c$ = 14.274 (4) Å, $\beta$ = 116.63 (2)°, $V$ = 2274 Å$^3$, and $\rho_{calcd}$ = 1.01 g/cm$^3$ for $Z$ = 4. I is situated about a crystallographic 2-fold axis passing through the center of the aza crown. Least-squares refinement based on 1016 observed reflections with intensities $I > 3\sigma(I)$ in the range $3.50° \le 2\theta \le 45.0°$ for I converged at $R$ = 0.039, $R_w$ = 0.049. The gallium compound (II), isostructural with I, crystallizes in the monoclinic space group $C2/c$ (No. 15) with unit cell parameters $a$ = 21.823 (8) Å, $b$ = 8.189 (1) Å, $c$ = 14.188 (2) Å, $\beta$ = 116.95 (6)°, $V$ = 2260 Å$^3$, and $\rho_{calcd}$ = 1.26 g/cm$^3$ for $Z$ = 4. Least-squares refinement based on 1570 observed reflections in the range $4.00° \le 2\theta \le 50.0°$ for II converged at $R$ = 0.056, $R_w$ = 0.060. The [14]aneN$_4$ aza crown assumed an unusual inverted basket conformation in I and II. Both I and II appear to be strained, as the two $M(CH_3)_3$ units and all four N–H units reside on the same side of the aza crown. The independent Al–N bond distance is 2.028 (3) Å, while the Ga–N bond distance is 2.124 (4) Å. Room-temperature reaction of I with 2 mol of trimethylgallium affords the heterobimetallic condensation compound $[Al(CH_3)]_2$[14]aneN$_4$$[Ga(CH_3)_3]_2$ (III). III crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with unit cell parameters $a$ = 8.195 (2) Å, $b$ = 13.783 (4) Å, $c$ = 11.162 (3) Å, $\beta$ = 90.70 (2)°, $V$ = 1261 Å$^3$, and $\rho_{calcd}$ = 1.34 g/cm$^3$ for $Z$ = 2. Least-squares refinement based on 1710 observed reflections with intensities $I > 3\sigma(I)$ in the range $3.50° \le 2\theta \le 50.0°$ converged at $R$ = 0.036, $R_w$ = 0.049. III resides about a crystallographic center of symmetry with a planar $Al_2N_2$ ring occupying the central cavity of the aza crown.

## Introduction

This laboratory has had an interest in the interactions of organoaluminum and organogallium species with macrocyclic amines for some time. Investigations in this regard have proven quite fruitful, as condensation reactions involving aluminum or gallium alkyls with aza crown ethers or multidentate open-chain amines have been shown to result in novel five-[1,2] and six-coordinate[3,4] organoaluminum and organogallium complexes. The aza crown ether [14]aneN$_4$, commonly referred to as cyclam (Figure 1), has figured prominently in the development of this chemistry. Another important aspect of organoaluminum and organogallium chemistry relative to macrocyclic ligands concerns the nonstoichiometric liquid inclusion compounds known as liquid clathrates, $[(CE)M'][M_2R_6X]$ (M = Al, Ga; R = alkyl; X = halide; CE = oxygen-based crown ether; M′ = alkali-metal ion).[5] It has been shown that $[MR_3]_n[CE]$ complexes can facilitate the preparation of liquid clathrates in the presence of appropriate alkali-metal salts.[6,7] While exploring the organoaluminum inclusion chemistry of aza crown ethers, we became intrigued with the interactions of organoaluminum units with aza hydrogen atoms of these ligands. It is well documented that room-temperature reaction of aluminum and gallium alkyls with primary and secondary amines typically results in the formation of simple adducts of the type $R_3N{\cdot}MR_3$[8,9] (M = Al, Ga), while condensation occurs at higher temperatures, giving rise to cage products possessing $M_2N_2$ fragments with extensive metal–nitrogen association.[10,11] Herein we report the syntheses and molecular structures of $[M(CH_3)_3]_2$[14]aneN$_4$ (M = Al (I), Ga (II)) and $[Al(CH_3)]_2$[14]aneN$_4$$[Ga(CH_3)_3]_2$ (III). Compounds I and II are novel, as they represent the first examples of an aza crown ether assuming an unusual inverted basket conformation with group 13 metals. III, isolated from reaction of I with $Ga(CH_3)_3$, is significant, as it represents the first structurally characterized heterobimetallic group 13 metal alkyl–aza crown ether complex. The X-ray crystal structure of I is provided in Figure 2, while that of III is provided in Figure 3.

## Experimental Section

Due to the extreme air and moisture sensitivity of the group 13 metal alkyls and the resulting reaction products, all manipulations were carried out by using standard Schlenk and glovebox techniques under purified argon or vacuum. The tetradentate aza crown ether [14]aneN$_4$ was prepared in our laboratory by a modification of the Ni(II) template synthesis offered by Barefield,[12] where the crude product was recrystallized from tetrahydrofuran (instead of chlorobenzene). Chlorobenzene and methylene chloride were distilled over $P_2O_5$ under an atmosphere of argon prior to use. Trimethylaluminum and trimethylgallium were generously donated by the Ethyl Corp. and used as received without further purification. $^1$H NMR spectra were recorded on a Bruker AC300 FT-NMR spectrometer. Melting points were measured in sealed capillaries and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

**$[Al(CH_3)_3]_2$[14]aneN$_4$ (I).** Inside the drybox, a reaction vessel was charged with [14]aneN$_4$ (4.98 mmol) and chlorobenzene (25 mL). The mixture was allowed to stir until the aza crown dissolved. Trimethylaluminum (9.98 mmol) was added slowly via syringe. The resulting slightly yellow solution was removed from the drybox and stirred at room temperature for 48 h. The solution was filtered via cannula into a 150-mL Schlenk flask. Reduction of solvent followed by cooling for several hours resulted in colorless, rectangular, extremely air-sensitive X-ray-quality crystals (80% yield based on [14]aneN$_4$). Mp: 172 °C. Anal. Calcd for $C_{16}H_{42}N_4Al_2$: C, 56.85; H, 12.21. Found: C, 58.54; H, 11.37. $^1$H NMR: $\delta$ 0.185 (s, 18 H, $(CH_3)_3Al$), 1.069 (m, 8 H, N*H*, $NCH_2CH_2CH_2N$), 1.457 (b s, 16 H, $NCH_2CH_2CH_2N$, $NCH_2CH_2N$).

**$[Ga(CH_3)_3]_2$[14]aneN$_4$ (II).** The reaction was carried out in a manner analogous to that for I. [14]aneN$_4$ (4.98 mmol) was allowed to react with trimethylgallium (4.98 mmol) in chlorobenzene (25 mL). The system was allowed to stir for 4 days. Cooling the concentrated solution to −15 °C resulted in colorless, square extremely air-sensitive X-ray-quality crystals (60% yield based on trimethylgallium). Mp: 145 °C. Anal. Calcd for $C_{16}H_{42}N_4Ga_2$: C, 44.69; H, 9.87. Found: C, 43.97;

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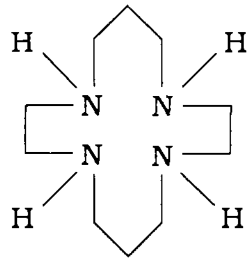

**Figure 1**. The tetradentate aza crown [14]ane$N_4$.

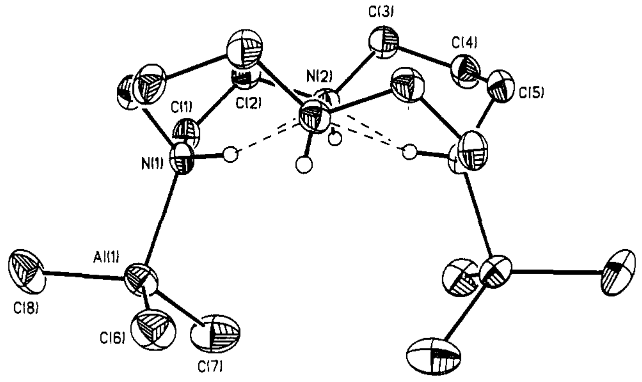

**Figure 2**. Thermal ellipsoid plot of $[Al(CH_3)_3]_2$[14]ane$N_4$ (I), showing the atom-labeling scheme. Thermal ellipsoids show 25% probability levels. All hydrogen atoms except those bonded to nitrogen have been omitted for clarity. Dashed lines indicate hydrogen-bonding interactions.

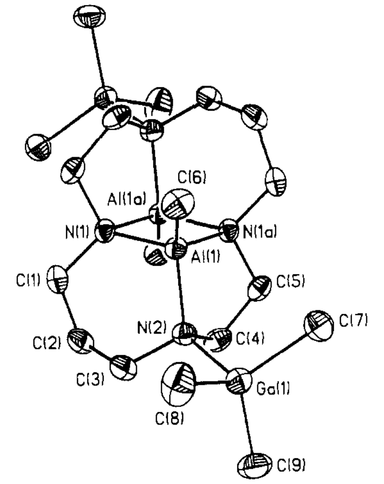

**Figure 3**. Thermal ellipsoid plot of $[AlCH_3]_2$[14]ane$N_4[Ga(CH_3)_3]_2$ (III), showing the atom-labeling scheme. Thermal ellipsoids show 35% probability levels. All hydrogen atoms have been omitted for clarity.

H, 9.95. $^1$H NMR: $\delta$ −0.568 (s, 18 H, $(CH_3)_3Ga$), 1.816 (b s, 8 H, N*H*, $NCH_2CH_2CH_2N$), 2.761 (b s, 16 H, $NCH_2CH_2CH_2N$, $NCH_2CH_2N$).

**$[Al(CH)_3]_2$[14]ane$N_4[Ga(CH_3)_3]_2$ (III).** A reaction vessel was charged with chlorobenzene, I (3.98 mmol), and trimethylgallium (2.00 mmol) in the drybox. The yellowish solution was capped and stirred for 48 h, upon which time a white precipitate formed. The solvent was removed in vacuo and the white powder dissolved in methylene chloride. Upon cooling to −15°C, a multitude of colorless, extremely air sensitive crystals resulted (74% yield based on I). Mp: 210 °C dec. Anal. Calcd for $C_{18}H_{44}N_4Al_2Ga_2$: C, 42.30; H, 8.62. Found: C, 40.87; H, 8.18. $^1$H NMR: $\delta$ 0.153 (s, 18 H, $(CH_3)_3Ga$), 0.295 (s, 6 H, $(CH_3)Al$), 0.895 (quintet, 4 H, $NCH_2CH_2CH_2N$), 1.244 (b s, 8 H, $NCH_2CH_2N$), 1.359 (b s, 8 H, $NCH_2CH_2CH_2N$).

**Crystal Structure Determination.** X-ray intensity data for I and III were collected on a Nicolet R3m/V diffractometer with an $\omega/2\theta$ scan technique. X-ray data for II were collected on an Enraf-Nonius CAD-4 diffractometer. Relevant crystallographic data for compounds I–III are given in Table I.

**$[Al(CH_3)_3]_2$[14]ane$N_4$ (I).** A colorless parallelepiped crystal of I was mounted in a thin-walled glass capillary under an inert atmosphere of argon. Cell parameters and an orientation matrix for data collection, obtained from a least-squares refinement of the setting angles of 38 carefully centered reflections in the range 24.80° < $2\theta$ < 33.98°, corresponded to a monoclinic cell. The space group was determined to be *C*2/*c* (No. 15). The structure was solved by direct methods and refined, on the basis of 1016 observed reflections with intensities $I > 3\sigma(I)$, by using SHELXTL.[13] Non-hydrogen atoms were refined by using anisotropic thermal parameters, and hydrogen atoms, by using isotropic thermal parameters. The weighting scheme was based on counting statistics and included a factor ($p$ = 0.0005) to downweight intense reflections. The peaks on the final difference map ranged from −0.13 to +0.14 e/Å$^3$. Least-squares refinement based on 1016 observed reflections with intensities $I > 3\sigma(I)$ in the range 3.50° ≤ $2\theta$ ≤ 45.0° for I converged at $R$ = 0.039, $R_w$ = 0.049. Final atomic coordinates are given in Table II. Selected bond distances and angles are given in Table III.

**$[Ga(CH_3)_3]_2$[14]ane$N_4$ (II).** A crystalline sample of II was prepared for analysis in a manner similar to that employed for I. Unit cell di-

**Table I**. Crystal Data for $[Al(CH_3)_3]_2$[14]ane$N_4$ (I), $[Ga(CH_3)_3]_2$[14]ane$N_4$ (II), and $[Al(CH_3)]_2$[14]ane$N_4[Ga(CH_3)_3]_2$ (III)

| | I | II | III |
|---|---|---|---|
| chem formula | $C_{16}H_{42}N_4Al_2$ | $C_{16}H_{42}N_4Ga_2$ | $C_{18}H_{44}N_4Al_2Ga_2$ |
| mol wt | 344.6 | 430.1 | 510.1 |
| space group (No.) | *C*2/*c* (15), monoclinic | *C*2/*c* (15), monoclinic | $P2_1/n$ (14), monoclinic |
| $a$, Å | 21.772 (4) | 21.823 (8) | 8.195 (2) |
| $b$, Å | 8.186 (2) | 8.189 (1) | 13.783 (4) |
| $c$, Å | 14.274 (4) | 14.188 (2) | 11.162 (3) |
| $\beta$, deg | 116.63 (2) | 116.95 (6) | 90.70 (2) |
| $V$, Å$^3$ | 2274 | 2260 | 1261 |
| $Z$ | 4 | 4 | 2 |
| $\rho_{calcd}$, g/cm$^3$ | 1.01 | 1.26 | 1.34 |
| radiation ($\lambda$, Å) | Mo K$\alpha$ (0.71073) | Mo K$\alpha$ (0.71073) | Mo K$\alpha$ (0.71073) |
| $T$, °C | | 21 | |
| $\mu$, cm$^{-1}$ | 1.27 | 25.11 | 22.08 |
| transm coeff | 0.97/1.00 | 0.74/1.00 | 0.90/1.00 |
| $R$ | 0.039 | 0.056 | 0.036 |
| $R_w$ | 0.049 | 0.060 | 0.049 |

**Table II**. Atomic Coordinates (×10$^4$) and Equivalent Isotropic Thermal Parameters (Å$^2$ × 10$^3$) for $[Al(CH_3)_3]_2$[14]ane$N_4$ (I)

| atom | $x$ | $y$ | $z$ | $U$(eq)[a] |
|---|---|---|---|---|
| Al(1) | 1441 (1) | 5677 (1) | 8064 (1) | 55 (1) |
| N(1) | 1070 (1) | 3374 (3) | 7676 (2) | 42 (1) |
| N(2) | −336 (1) | 2427 (4) | 6058 (2) | 47 (1) |
| C(1) | 863 (2) | 3079 (5) | 6542 (3) | 52 (2) |
| C(2) | 296 (2) | 1851 (5) | 6050 (3) | 53 (2) |
| C(3) | −887 (2) | 1199 (5) | 5644 (4) | 63 (2) |
| C(4) | −1545 (2) | 1814 (6) | 5620 (3) | 61 (2) |
| C(5) | −1534 (2) | 2043 (5) | 6676 (3) | 56 (2) |
| C(6) | 1553 (3) | 6185 (7) | 9477 (4) | 81 (3) |
| C(7) | 717 (5) | 7046 (9) | 6992 (6) | 105 (4) |
| C(8) | 2298 (3) | 5608 (9) | 7913 (5) | 91 (3) |

[a] Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

**Table III**. Bond Distances (Å) and Angles (deg) for $[Al(CH_3)_3]_2$[14]ane$N_4$ (I)

| | | | |
|---|---|---|---|
| | Distances | | |
| Al(1)–N(1) | 2.028 (3) | Al(1)–C(6) | 1.965 (6) |
| Al(1)–C(7) | 1.979 (7) | Al(1)–C(8) | 1.973 (8) |
| N(1)–C(1) | 1.493 (5) | N(1)–C(5A) | 1.492 (4) |
| N(2)–C(2) | 1.459 (5) | N(2)–C(3) | 1.472 (5) |
| C(1)–C(2) | 1.501 (5) | C(3)–C(4) | 1.504 (7) |
| C(4)–C(5) | 1.508 (7) | C(5)–N(1A) | 1.492 (4) |
| | Angles | | |
| N(1)–Al(1)–C(6) | 109.1 (2) | N(1)–Al(1)–C(7) | 103.5 (2) |
| C(6)–Al(1)–C(7) | 111.3 (3) | N(1)–Al(1)–C(8) | 102.9 (2) |
| C(6)–Al(1)–C(8) | 115.5 (3) | C(7)–Al(1)–C(8) | 113.4 (4) |
| Al(1)–N(1)–C(1) | 109.6 (2) | Al(1)–N(1)–C(5A) | 115.7 (2) |
| C(1)–N(1)–C(5A) | 110.2 (3) | C(2)–N(2)–C(3) | 112.3 (3) |
| N(1)–C(1)–C(2) | 113.7 (4) | N(2)–C(2)–C(1) | 111.1 (3) |
| N(2)–C(3)–C(4) | 112.2 (4) | C(3)–C(4)–C(5) | 115.5 (3) |
| C(4)–C(5)–N(1A) | 114.4 (4) | | |

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**Table IV.** Final Fractional Coordinates for $[Ga(CH_3)_3]_2[14]aneN_4$ (II)

| atom | $x/a$ | $y/b$ | $z/c$ | $B$(eqv)[a] |
|---|---|---|---|---|
| Ga | 0.85443 (3) | 0.07501 (8) | 0.69103 (5) | 4.38 (1) |
| N(1) | 0.8945 (2) | −0.1650 (6) | 0.7333 (3) | 3.2 (1) |
| N(2) | 0.9653 (2) | −0.2573 (6) | 0.6037 (3) | 3.6 (1) |
| C(1) | 0.8471 (3) | −0.2995 (8) | 0.6672 (5) | 4.5 (1) |
| C(2) | 0.8450 (3) | −0.3199 (8) | 0.5617 (5) | 4.8 (2) |
| C(3) | 0.9107 (3) | −0.3794 (8) | 0.5634 (4) | 4.6 (1) |
| C(4) | 0.9717 (3) | −0.3129 (8) | 0.8966 (4) | 4.2 (1) |
| C(5) | 0.9143 (3) | −0.1915 (8) | 0.8463 (4) | 4.1 (1) |
| C(6) | 0.8443 (4) | 0.123 (1) | 0.5488 (5) | 6.4 (2) |
| C(7) | 0.7708 (4) | 0.063 (1) | 0.7071 (6) | 7.5 (2) |
| C(8) | 0.9308 (6) | 0.204 (1) | 0.8008 (7) | 9.4 (3) |

[a] $B(\mathrm{eqv}) = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

**Table V.** Selected Bond Distances (Å) and Angles (deg) for $[Ga(CH_3)_3]_2[14]aneN_4$ (II)

| | | | |
|---|---|---|---|
| | Distances | | |
| Ga–N(1) | 2.124 (4) | N(1)–C(5) | 1.476 (7) |
| Ga–C(6) | 1.966 (8) | N(2)–C(3) | 1.459 (7) |
| Ga–C(7) | 1.94 (1) | C(1)–C(2) | 1.49 (1) |
| Ga–C(8) | 1.991 (9) | C(2)–C(3) | 1.50 (1) |
| N(1)–C(1) | 1.512 (7) | C(4)–C(5) | 1.502 (8) |
| | Angles | | |
| N(1)–Ga–C(6) | 108.3 (3) | Ga–N(1)–C(5) | 108.8 (4) |
| N(1)–Ga–C(7) | 102.0 (3) | C(1)–N(1)–C(5) | 110.3 (5) |
| N(1)–Ga–C(8) | 100.3 (3) | N(1)–C(1)–C(2) | 113.9 (6) |
| C(6)–Ga–C(7) | 117.1 (3) | C(1)–C(2)–C(3) | 115.2 (4) |
| C(6)–Ga–C(8) | 111.2 (4) | N(2)–C(3)–C(2) | 112.8 (5) |
| C(7)–Ga–C(8) | 115.7 (5) | N(1)–C(5)–C(4) | 112.6 (5) |
| Ga–N(1)–C(1) | 114.9 (3) | | |

mensions and an orientation matrix for data collection, obtained from a least-squares refinement of the setting angles of 25 carefully centered reflections in the range 12.15° $< 2\theta <$ 15.73°, indicated a monoclinic system. The space group was determined to be $C2/c$ (No. 15); II was found to be isostructural with I. The structure was solved by direct methods and refined on the basis of 1570 observed reflections. The amine hydrogen atoms were located from a difference map; all other hydrogen atoms were placed in idealized positions ($d_{C-H}$ = 0.95 Å). Hydrogen atoms were assigned isotropic thermal parameters 20% greater than the equivalent isotropic values of their host atoms. The peaks on the final difference map ranged from −0.223 to +0.823 e/Å$^3$. Non-hydrogen atoms were refined by using anisotropic thermal parameters. Least-squares refinement based on 1570 observed reflections in the range 4.00° $\leq 2\theta \leq$ 50.0° for II converged at $R$ = 0.056, $R_w$ = 0.060. Final atomic coordinates are given in Table IV. Selected bond distances and angles are given in Table V.

**$[Al(CH_3)]_2[14]aneN_4[Ga(CH_3)_3]_2$ (III).** A single-crystalline sample of III was prepared for X-ray examination in the same manner as employed for I and II. Cell parameters and an orientation matrix, determined from the setting angles of 50 carefully centered reflections in the range 28.12° $< 2\theta <$ 38.53°, afforded a monoclinic cell. The space group was determined to be $P2_1/n$ (No. 14). As with I, the structure was solved by direct methods. Non-hydrogen atoms were refined by using anisotropic thermal parameters. Hydrogen atoms were located by standarded difference Fourier techniques. All hydrogen atoms except those bonded to atom C(6) were refined by using isotropic thermal parameters. The hydrogen atoms bonded to atom C(6) were determined to be disordered about two equally occupied sites; these hydrogen half-atoms were included in the structure factor calculation at their difference map positions and were allowed to ride on atom C(6). An isotropic group thermal parameter ($U_{iso}$ = 0.05 (1) Å$^2$) was refined for all of the hydrogen half-atoms. The weighting scheme was based on counting statistics and included a factor ($p$ = 0.001) to downweight the intense reflections. The peaks on the final difference map ranged from −0.73 to +0.41 e/Å$^3$. Least-squares refinement based on 1710 observed reflections with intensities $I > 3\sigma(I)$ in the range 3.50° $\leq 2\theta \leq$ 50.0° converged at $R$ = 0.036, $R_w$ = 0.049. Final atomic coordinates are given in Table VI. Selected bond distances and angles are given in Table VII.

**Table VI.** Atomic Coordinates (×10$^4$) and Equivalent Isotropic Thermal Parameters (Å$^2$ × 10$^3$) for $[Al(CH_3)]_2[14]aneN_4[Ga(CH_3)_3]_2$ (III)

| atom | $x$ | $y$ | $z$ | $U$(eq)[a] |
|---|---|---|---|---|
| Ga(1) | 1012 (1) | 1890 (1) | 5149 (1) | 47 (1) |
| Al(1) | −652 (1) | 4090 (1) | 5088 (1) | 32 (1) |
| N(1) | −792 (3) | 5134 (2) | 3915 (3) | 36 (1) |
| N(2) | 1089 (3) | 3343 (2) | 4487 (3) | 40 (1) |
| C(1) | −483 (5) | 4818 (3) | 2656 (3) | 48 (1) |
| C(2) | 1061 (6) | 4239 (4) | 2495 (4) | 52 (1) |
| C(3) | 1097 (6) | 3273 (3) | 3157 (4) | 52 (1) |
| C(4) | 2629 (4) | 3814 (3) | 4924 (4) | 49 (1) |
| C(5) | 2355 (4) | 4296 (3) | 6119 (4) | 46 (1) |
| C(6) | −2720 (5) | 3551 (3) | 5585 (4) | 54 (1) |
| C(7) | 719 (7) | 2009 (5) | 6904 (5) | 62 (2) |
| C(8) | −876 (10) | 1292 (5) | 4283 (7) | 83 (2) |
| C(9) | 3166 (9) | 1369 (5) | 4669 (6) | 77 (2) |

[a] Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

**Table VII.** Bond Lengths (Å) and Angles (deg) for $[Al(CH_3)]_2[14]aneN_4[Ga(CH_3)_3]_2$ (III)

| | | | |
|---|---|---|---|
| | Distances | | |
| Ga(1)–N(2) | 2.136 (3) | Ga(1)–C(7) | 1.983 (5) |
| Ga(1)–C(8) | 1.993 (8) | Ga(1)–C(9) | 1.986 (7) |
| Al(1)–N(1) | 1.949 (3) | Al(1)–N(2) | 1.888 (3) |
| Al(1)–C(6) | 1.938 (4) | Al(1)–N(1A) | 1.937 (3) |
| N(1)–C(1) | 1.496 (5) | N(1)–C(5A) | 1.502 (5) |
| N(2)–C(3) | 1.488 (5) | N(2)–C(4) | 1.496 (5) |
| C(1)–C(2) | 1.509 (6) | C(2)–C(3) | 1.522 (7) |
| C(4)–C(5) | 1.509 (6) | | |
| | Angles | | |
| N(2)–Ga(1)–C(7) | 105.6 (2) | N(2)–Ga(1)–C(8) | 104.2 (2) |
| C(7)–Ga(1)–C(8) | 114.3 (3) | N(2)–Ga(1)–C(9) | 102.5 (2) |
| C(7)–Ga(1)–C(9) | 114.5 (3) | C(8)–Ga(1)–C(9) | 114.0 (3) |
| N(1)–Al(1)–N(2) | 101.7 (1) | N(1)–Al(1)–C(6) | 115.5 (2) |
| N(2)–Al(1)–C(6) | 124.1 (2) | N(1)–Al(1)–N(1A) | 90.5 (1) |
| N(2)–Al(1)–N(1A) | 92.7 (1) | C(6)–Al(1)–N(1A) | 125.3 (2) |
| AL(1)–N(1)–C(1) | 114.0 (3) | Al(1)–N(1)–Al(1A) | 89.5 (1) |
| C(1)–N(1)–Al(1A) | 126.3 (2) | Al(1)–N(1)–C(5A) | 116.5 (2) |
| C(1)–N(1)–C(5A) | 106.4 (3) | Al(1A)–N(1)–C(5A) | 103.9 (2) |
| Ga(1)–N(2)–Al(1) | 111.3 (1) | Ga(1)–N(2)–C(3) | 106.6 (3) |
| Al(1)–N(2)–C(3) | 113.7 (2) | Ga(1)–N(2)–C(4) | 108.8 (2) |
| Al(1)–N(2)–C(4) | 106.6 (2) | C(3)–N(2)–C(4) | 109.8 (3) |
| N(1)–C(1)–C(2) | 114.7 (3) | C(1)–C(2)–C(3) | 114.6 (4) |
| N(2)–C(3)–C(2) | 115.3 (4) | N(2)–C(4)–C(5) | 110.2 (3) |
| C(4)–C(5)–N(1A) | 110.2 (3) | | |

## Results and Discussion

Several points are worthy of note regarding structure and bonding in compounds I and II. Each molecule appears to be strained, as both $M(CH_3)_3$ (M = Al, Ga) units and all four aza hydrogen atoms reside on the same side of the $N_4$ plane of the aza crown (Figure 2). Each of these complexes resides about a 2-fold axis of rotation passing through the center of the aza crown. On the basis of an X-ray crystal structure, the uncomplexed [14]ane$N_4$ aza crown was shown to reside in an endodentate conformation.[14] Moreover, the endodentate conformation of [14]ane$N_4$ was shown to be stabilized by hydrogen bonding, as two aza hydrogen atoms were directed toward the center of the macrocyclic cavity while the remaining two aza hydrogen atoms were directed above and below the $N_4$ plane. Considering the presence of two group 13 metal alkyl units associated with [14]ane$N_4$ in I and II, it is interesting that the aza crown is in an endodentate conformation. As with the uncomplexed ligand, the endodentate conformation of [14]ane$N_4$ in I and II may also be regarded as a consequence of weak intramolecular hydrogen bonding. The orientation of the aza hydrogen atoms in I and II is worthy of note. Distinctly different from the conformation observed in the uncomplexed ligand, all four aza hydrogen atoms in I and II are shown to reside on the same side of the $N_4$ plane. Cross-ring N···N contacts across the ethylene bridges are 2.995 (5) and 2.981 (6) Å and those across the propylene bridges are 3.005 (5) and 2.983 (6) for I and II, respectively. The Al–N bond distance is 2.028 (3) Å for I, while the Ga–N bond distance is

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2.124 (4) Å for II. The environment around each metal atom is essentially tetrahedral, with average C–Al–C and N–Al–C bond angles of 113.4 (2) and 105.2 (3)° and C–Ga–C and N–Ga–C bond angles of 114.3 (2) and 104.0 (3)°, respectively.

The fact that one would have expected I and II to have assumed a sterically less demanding trans conformation instead of the observed sterically crowded cis conformation is noteworthy and warrants closer examination. In this regard, it is interesting to consider two factors: (a) the dimeric nature of $M(CH_3)_3$ (M = Al, Ga) and (b) inversion of heterocyclic ring systems containing N–H fragments. Although the reaction chemistry of trimethylaluminum and trimethylgallium is largely dominated by monomeric units, these species are generally regarded to be predominantly dimeric in solution, being bridged by two $\mu$-methyl groups.[15,16] In terms of the second factor, room-temperature inversion of heterocyclic ring systems containing N–H moieties is well documented.[17,18] Thus, it is reasonable that the endodentate conformation of $[14]aneN_4$ in I and II, while certainly stabilized by hydrogen bonding, was effectively trapped as it was approached by the dimeric form of the group 13 metal alkyl, $M_2(CH_3)_6$ (M = Al, Ga). The dimer could then be cleaved as each metal alkyl center approached nitrogen atoms on the same side of the azacrown.

Compound III results from the room-temperature reaction of I with 2 mol of trimethylgallium. The two $Ga(CH_3)_3$ units form adducts with two of the nitrogen atoms of the aza crown while the two trimethylaluminum units originally present in I participate in condensation with the aza hydrogen atoms of the aza crown. The most striking feature of III is the formation of the planar $Al_2N_2$ ring within the central cavity of the macrocycle and the formation of trimethylgallium adducts on the exterior of the macrocycle (Figure 3). The mean Al–N bond distance within the planar $Al_2N_2$ ring of 1.943 (8) Å compares to 1.888 (3) Å for the out-of-plane Al(1)–N(2) bond. The Ga(1)–N(2) bond distance is 2.136 (3) Å. The Al–N–Al and N–Al–N bond angles are 89.5 (1) and 92.67 (2)°, respectively. Compound III is very similar structurally to the condensation product $[Al(CH_3)]_2$-$[14]aneN_4[Al(CH_3)_3]_2$ (IV), a compound isolated from reaction of $[14]aneN_4$ with 4 mol of $Al(CH_3)_3$.[19] Interestingly, although III and IV proved to be isostructural, the twinning that occurred for IV was not observed for the heterobimetallic complex, III. Heating of I has been shown to produce IV in low yield. It appears that the first two $Al(CH_3)_3$ units that react with the aza crown become involved in the condensation while subsequently added $Ga(CH_3)_3$ species form adducts with the two remaining nitrogen atoms. Thus, it is reasonable to consider the greater Lewis acidity of trimethylaluminum (relative to trimethylgallium) as a contributing factor in the preparation of III.

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**Supplementary Material Available:** Tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters and summaries of data collection and refinement (23 pages); listings of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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# Cage Opening of Parent Closo Cage Carboranes with Fluoride Ion: Formation of $[5\text{-F-}\textit{nido}\text{-}2,4\text{-}C_2B_4H_6]^-$

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Fluoride ion, in aprotic solvents, has been found to be effective in the cage opening of *closo*-carboranes such as 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, 1,2-$C_2B_{10}H_{12}$, and 1,7-$C_2B_{10}H_{12}$. Nearly quantitative conversion to *nido*-carboranes is observed; in the case of 1,6-$C_2B_4H_6$ the product is the $[5\text{-F-}\textit{nido}\text{-}2,4\text{-}C_2B_4H_6]^-$ ion. In the case of the higher carboranes the *nido*-carborane produced is that expected from the removal of a single vertex boron.

## Introduction

Previous studies in our laboratories[1,2] demonstrated that fluoride ion can displace higher halogens in appropriately substituted *closo*-2,4-$C_2B_5H_7$ derivatives. Recently, we have discovered that it is not necessary to have a halogen attached to the cage of a *closo*-carborane in order for a reaction to be initiated with fluoride ion.[3] This report discusses the results of reactions involving the *closo*-carboranes 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, and 1,2- and 1,7-$C_2B_{10}H_{12}$.

## Experimental Section

**Materials and Handling of Chemicals.** The reagents, (a) tetrabutylammonium fluoride (TBAF), as the trihydrate, (b) TBAF, as a 1 M solution in tetrahydrofuran (THF), (c) $CaH_2$, (d) deuterated THF, and (e) deuterated acetonitrile, were all obtained from Aldrich Chemical Co. The TBAF/THF solution was dried over $CaH_2$; the dried solution had to be used within several days, otherwise it separated into two phases (only the lower layer, a light tan color, appeared to contain fluoride ion, as assessed from fluorine-19 NMR spectroscopy and also by its reaction toward 1,6-$C_2B_4H_6$; vide infra). Upon the drying of TBAF/acetonitrile solutions with $CaH_2$, the solution remained as one layer. Standard high-vacuum and drybag techniques were employed in the handling of all chemicals.

**Nuclear Magnetic Resonance.** Proton (400.135 MHz), boron-11 (128.379 MHz), and fluorine-19 (376.503 MHz) spectra were gathered by using a Bruker AM400 FT-NMR instrument; the spectra were referenced to TMS, $Et_2O{\cdot}BF_3$, and $CFCl_3$, respectively, with negative chemical shift values upfield.

**Reaction of TBAF with *closo*-1,6-$C_2B_4H_6$. Using THF as Solvent.** A dried TBAF/THF solution (0.5 mL, 0.5 mmol of TBAF) was combined with *closo*-1,6-$C_2B_4H_6$ (0.25 mmol). After 1 h at room temperature about 90% of 1,6-$C_2B_4H_6$ disappeared, as monitored by $^{11}B$ NMR spectroscopy, with the concomitant formation of the $[5\text{-F-}\textit{nido}\text{-}2,4\text{-}C_2B_4H_7]^-$ ion. After 17 days, the NMR spectrum of the solution showed essentially quantitative conversion to the $[5\text{-F-}\textit{nido}\text{-}2,4\text{-}C_2B_4H_7]^-$ ion with no observable boron impurities in the boron-11 NMR spectrum. The $^{11}B$ NMR resonances assigned to the $[5\text{-F-}\textit{nido}\text{-}2,4\text{-}C_2B_4H_7]^-$ ion are as follows: $\delta = -50.83$, $J(BH) = 158$ Hz, for B(1); $\delta = -9.75$, $J(BH_t) = 136$ Hz, $J(BH_\mu) =$ ca. 40 Hz, for B(6); $\delta = +17.9$ (broad singlet) for B(3); $\delta = +20.52$, $J(^{11}B^{19}F) =$ ca. 60 Hz, $J(BH_\mu) =$ ca. 45 Hz, for B(5) (note: the bridging hydrogen couplings to boron were obtained from resolution-enhanced spectra). Proton NMR data: $\delta = -2.22$, broad, for

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