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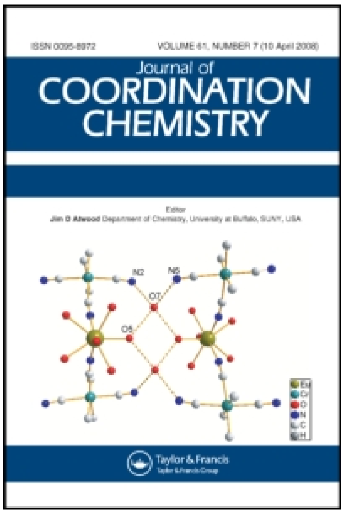

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Participation of Methylene Chloride in Organo-Group 13 Systems. Synthesis and Molecular Structure of $[(C_4H_9)_2Al\{N(CH_2CH_2O)_3\}Al(Cl)]_2$ and $[(CH_3)Ga\cdot[14]aneN_4]Cl_2$

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PARTICIPATION OF METHYLENE CHLORIDE IN ORGANO-GROUP 13 SYSTEMS. SYNTHESIS AND MOLECULAR STRUCTURE OF $[(C_4H_9)_2Al\{N(CH_2CH_2O)_3\}Al(Cl)]_2$ AND $[(CH_3)Ga\cdot[14]aneN_4]Cl_2$

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The organoaluminum complex $[(C_4H_9)_2Al\{N(CH_2CH_2O)_3\}Al(Cl)]_2$, I, was prepared by reaction of an excess of $(i\text{-}C_4H_9)_2AlH$ with triethanolamine, $N(CH_2CH_2OH)_3$. I crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters $a=10.246(4)$, $b=12.864(4)$, $c=14.681(6)$ Å, $\alpha=104.96(3)$, $\beta=89.92(3)$, $\gamma=96.84(3)^\circ$, $V=1855$ Å^3 and $D_c=1.24\,g\,cm^{-3}$ for $Z=2$. Least-squares refinement based on 3745 observed reflections with intensities $I>3\sigma(I)$ in the range $3.50<2\theta<45.0^\circ$ converged at $R=0.080$, $R_w=0.099$. I contains two triethanolamine ligands bridged by four Al fragments. The two core Al atoms are six-coordinate residing in octahedral environments. The mean Al–C distance in I is 1.978(9) Å while the Al–O distances range from 1.798(4) to 1.931(5) Å. The crystalline product $[(CH_3)Ga\cdot[14]aneN_4]Cl_2$, II, isolated from reaction of $(CH_3)_3Ga$ with $[14]aneN_4$, crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters $a=13.853(5)$, $b=10.755(4)$, $c=13.147(5)$ Å, $\beta=113.80(3)^\circ$ $V=1792$ Å^3 and $D_c=1.48\,g\,cm^{-3}$ for $Z=4$. Least-squares refinement based on 1832 observed reflections with intensities $I>3\sigma(I)$ in the range $3.50<2\theta<45.0^\circ$ converged at $R=0.076$, $R_w=0.100$. The Ga atom associated with the macrocycle is six-coordinate residing in a distorted octahedral environment. The mean Ga–N distance in II is 2.08(1) Å while the Ga–C bond distance is 1.982(14) Å. The chlorine atoms observed in I and II appear to have resulted from solvent participation of methylene chloride.

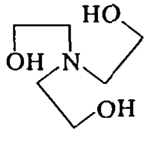
Keywords: Aluminum alkyl, gallium alkyl, amine, octahedral, X-ray structure

INTRODUCTION

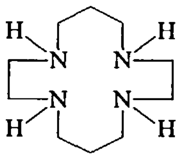
Solvent participation in organoaluminum system has been observed for some time. Acetonitrile is a particularly informative example. In 1965, Jennings *et al.*[1] reported a series of organoaluminum-acetonitrile addition products and their thermal nitrile rearrangement to alkylideneamino-dialkylaluminum species $(R'RCN\cdot AlR'_2)_2$ (R = Me, R′ = Me, Et, Bu). Similar species were isolated by Atwood *et al.* in the thermolysis of $[Al_2(CH_3)_6SCN]$.[2] Participation of acetonitrile in organoaluminum systems has also been observed in this laboratory as reaction of trimethylaluminum with tris(2-aminoethyl)amine (tren) afforded $[(tren)Al(CH_3CN)_6]$.[3]

The α-elimination of hydrogen chloride from methylene chloride has been shown to occur in the presence of strong bases.[4] Also, crown ether catalysts have been used to promote α-elimination from chloroform and other haloalkanes producing hydrogen halide.[5] In an effort to investigate the effect of chlorinated solvents on group 13 metal alkyl systems, this study was undertaken. In this contribution we report the synthesis and structure of $[Al(C_4H_9)_2\{N(CH_2CH_2O)_3\}Al(Cl)]_2$, I, and

$[(CH_3)Ga\cdot[14]aneN_4]Cl_2$, **II**. Compound **I** results from reaction of triethanolamine (a) with diisobutylaluminum hydride in a methylene chloride/acetonitrile solvent mixture. Compound **II** was isolated from reaction of trimethylgallium with $[14]aneN_4$ (b) in a toluene/methylene chloride solvent mixture. Both compounds **I** and **II** result from reactions involving solvent participation of methylene chloride.



(a)



(b)

EXPERIMENTAL

General

Standard Schlenk technique was employed in conjunction with an inert atmosphere dry box (Vacuum Atmospheres HE-43 Dri-Lab). Triethanolamine, purchased from Aldrich Chemical Co., was used as received. Trimethylgallium and diisobutylaluminum hydride were procured from Ethyl Corp. The macrocyclic tetradentate secondary amine, $[14]aneN_4$, was prepared by the Ni-template method described by Barefield *et al.*[6] ^1H and ^{27}Al NMR data were recorded on a Bruker AC-300-P NMR spectrometer. Single crystal X-ray data were collected on a Nicolet R3m/V diffractometer.

Synthesis of $[Al(C_4H_9)_2\{N(CH_2CH_2O)_3\}Al(Cl)]_2$, *I*

Inside the dry box a reaction vessel was charged with triethanolamine, $N(CH_2CH_2OH)_3$, (6.20 mmol) and a methylene chloride/acetonitrile solvent mixture (10 cm^3 and 5 cm^3, respectively). Diisobutylaluminum hydride (15.5 mmol) was slowly added *via* syringe. Reaction was immediate and exothermic. The reaction vessel was removed from the dry box and heated in an oil bath (100°C) for 24 h. Throughout the heating cycle the reaction vessel was vented frequently. Upon cooling, a multitude of small, colourless, extremely air sensitive crystals were obtained from a light brown solution (80% based on triethanolamine). ^1H NMR ($CDCl_3$): δ 0.962 (d, 24H, $AlCH_2CH(CH_3)_2)$), 1.88 (m, 4H, $AlCH_2CH(CH_3)_2$), -0.065 (d, 8H, $AlCH_2CH(CH_3)_2$), 3.00, 3.63, 3.92, 4.04 (multiplets, 24H, $N(CH_2)_2O$). ^{27}Al NMR ($CDCl_3$): δ 32.6 (s).

Synthesis of $[(CH_3)Ga.[14]aneN_4]Cl_2$, *II*

A reaction vessel was charged with $[14]aneN_4$ (5 mmol) and $(CH_3)_3Ga$ (5.0 mmol) in toluene. The resulting solution was heated in an oil bath (90°C) for 24 hours. The system was vented frequently. Methylene chloride (5 cm^3) was then added for the recrystallization process. The resulting light yellow solution was allowed to stand undisturbed for several hours at room temperature. A multitude of small, colourless, air-sensitive crystals was obtained in quantitative yield, m.p. 214°C (dec). ^1H NMR ($CDCl_3$): δ −0.34 (s, 3H, Ga(CH_3)), 1.79 (bs, 8H, $NCH_2CH_2CH_2N$, NH), 2.91 (bs, 16H, $N(CH_2)_2N$, $NCH_2CH_2CH_2N$).

Structural solution and refinement

$[(C_4H_9)_2Al\{N(CH_2CH_2O)_3\}Al(Cl)]_2$, *I*

A single crystal of $[Al(C_4H_9)_2\{N(CH_2CH_2O)_3\}Al(Cl)]_2$, **I**, was mounted in a thin-walled glass capillary under an atmosphere of argon in the dry box. Cell parameters and an orientation matrix for data collection, obtained from a least-squares analysis of the setting angles of 35 carefully centred reflections in the range $15.14 < 2\theta < 29.79°$, corresponded to the triclinic space group $P\bar{1}$, with two molecules per unit cell. The asymmetric unit consists of two half-molecules, each of which is situated about an inversion centre (molecule one—Cl(1)–C(14) is situated about an inversion centre at (0, 0, 0); molecule two—Cl(2)–C(28) is situated about an inversion centre at (0.5, 0.5, 0.5). The two unique molecules in the unit cell have essentially identical conformations for the core atoms, but differ in the conformation of the isobutyl groups. The structure was solved by direct methods and refined, based on 3745 observed reflections using SHELXTL.[7] Anisotropic thermal parameters were used for non-hydrogen atoms. Hydrogen atoms were located by standard difference Fourier techniques and were included in the structure factor calculated at optimized positions ($d_{C-H} = 0.96$ Å). Separate isotropic group thermal parameters were refined for the methylene carbon atoms of the amine groups ($U_{iso} = 0.050(4)$ Å^2) and for the carbon atoms of the isobutyl groups ($U_{iso} = 0.095(8)$ Å^2). Two isobutyl groups were disordered: atoms C(12a) and (C14a) (multiplicity = 0.26) and C(25a). C(26a), and C(28a) (multiplicity = 0.36) represent minor occupancy sites for their corresponding unlettered counterparts. The multiplicities were determined by refinement, but were held at fixed values during the final cycles of refinement. Refinement converged at $R = 0.080$, $R_w = 0.099$. The weighting scheme was based on counting statistics and included a factor ($p = 0.00015$) to downweight the intense reflections. Peaks on the final difference map ranged from −0.84 to 1.06 $e^-/Å^3$. Relevant crystallographic data are given in Table I. Final fractional atomic coordinates are given in Table II. Selected bond distances and angles are provided in Table III.

$[(CH_3)Ga.[14]aneN_4]Cl_2$, *II*

A single crystal of $[(CH_3)Ga\cdot[14]aneN_4]Cl_2$, **II**, was mounted in a thin-walled glass capillary under an atmosphere of argon in the dry box. Cell parameters and an orientation matrix for data collection, obtained from a least-squares analysis of the setting angles of 42 carefully centred reflections in the range $28.44 < 2\theta < 39.38°$, corresponded to the monoclinic system. The compound crystallizes in the space group $P2_1/c$ with four molecules per unit cell. The structure was solved by direct methods and refined, based on 1832 observed reflections, using SHELXTL. Anisotropic thermal parameters were used for non-hydrogen atoms. Amine and methylene hydrogen atoms were located by standard difference Fourier techniques and were included in the structure factor calculation at optimized positions ($d_{C-H} = 0.96$ Å), and were allowed to ride on the atom to which they were bounded. An isotropic group thermal parameter ($U_{iso} = 0.047(7)$ Å^2) was refined for all of these hydrogen atoms. Refinement converged at $R = 0.076$, $R_w = 0.100$. The weighting scheme was based on counting statistics and included a factor ($p = 0.0005$) to downweight the intense reflections. Peaks on the

TABLE I
Summary of the crystallographic data for $[(C_4H_9)_2Al\{N(CH_2CH_2O)_3\}Al(Cl)]_2$, **I**, and $[(CH_3)Ga.[14]aneN_4]Cl_2$, **II**.

	I	II
Empirical formula	$C_{28}H_{56}N_2O_6Al_4Cl_2$	$C_{11}H_{27}N_4GaCl_2$
Molecular weight	695.59	355.99
Colour; habit	colourless; parallelepiped	
Space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
a, Å	10.246(4)	13.853(5)
b, Å	12.864(4)	10.755(4)
c, Å	14.681(6)	13.147(5)
α, °	104.96(3)	
β, °	89.92(3)	113.80(3)
γ, °	96.84(3)	
Cell volume, Å^3	1855	1792
Z	2	4
D_c, g cm^{-3}	1.24	1.48
Diffractometer	Nicolet R3m/V	
Radiation	Mo-Kα (λ=0.71073 Å)	
Temperature	21°C	
2θ Range, deg	3.50 to 45.0	
Reflections collected	5071	2610
Reflections observed	3745	1832
GOF	3.28	3.25
R	0.080	0.076
R_w	0.099	0.100

final difference map ranged from -0.88 to $2.29\,e^-/Å^3$. Relevant crystallographic data are given in Table I. Final atomic coordinates are listed in Table IV. Selected bond distances and angles are provided in Table V.

RESULTS AND DISCUSSION

The X-ray crystal structure of **I** is shown in Figure 1. Several points are worthy of note regarding structure and bonding in **I**. The molecule resides about a crystallographic centre of symmetry coincident with the centre of an Al_2O_2 four-membered ring. Two triethanolamine units bridged by four aluminum fragments results in an Al_4O_6 aggregate. This moiety is composed of two fused six-membered Al_3O_3 rings in which each oxygen atom bridges two aluminum atoms. While the mechanism leading to **I** is unclear, certainly the presence of the two chlorine atoms results from solvent participation of methylene chloride.

Particularly significant is the fact that the core aluminum atoms, Al(1) and Al(1a), are six-coordinate. The coordination sphere of each core aluminum atom consists of four oxygen atoms, one nitrogen atom, and a chlorine atom. The Al(1) atom is coplanar with N(1), Cl(1), O(2), O(2a), while the two remaining oxygen atoms, O(1) and O(3), reside in axial positions relative to this plane. The relevant bond angles about Al(1), O(3)-Al(1)-O(1), N(1)-Al(1)-O(2a) and Cl(1)-Al(1)-O(2), are 164.2(2),

TABLE II
Final fractional atomic coordinates (× 10^4) for $[(C_4H_9)_2Al\{N(CH_2CH_2O)_3\}Al(Cl)]_2$, I.

Atoms	*x/a*	*y/b*	*z/c*	*U(eq)**
Cl(1)	2771(2)	426(1)	−1268(1)	44(1)
Al(1)	1348(2)	377(1)	−114(1)	25(1)
Al(2)	−713(2)	2233(2)	295(1)	33(1)
O(1)	960(4)	1830(3)	51(3)	32(2)
O(2)	72(4)	317(3)	822(3)	29(1)
O(3)	1816(4)	−957(3)	90(3)	33(2)
N(1)	2600(5)	1079(4)	978(3)	35(2)
C(1)	2058(7)	2630(5)	426(5)	46(3)
C(2)	3151(7)	2131(5)	814(5)	41(3)
C(3)	601(7)	432(5)	1742(4)	38(2)
C(4)	1833(7)	1244(5)	1866(4)	38(2)
C(5)	2913(7)	−833(6)	735(5)	42(3)
C(6)	3612(7)	322(6)	932(5)	43(3)
C(7)	−864(7)	2829(5)	1670(5)	43(3)
C(8)	−1953(8)	3538(6)	2009(5)	51(3)
C(9)	−1852(10)	4064(7)	3070(6)	75(4)
C(10)	−3302(9)	2872(8)	1734(7)	80(4)
C(11)	−1062(8)	3278(6)	−429(5)	51(3)
C(12)	−862(12)	3167(8)	−1489(8)	49(4)
C(13)	−1068(10)	4247(7)	−1719(6)	73(4)
C(14)	428(20)	2820(18)	−1793(12)	89(8)

* Equivalent isotropic *U* (× 10^3) defined as one third of the trace of the orthogonalized U_{ij} tensor.

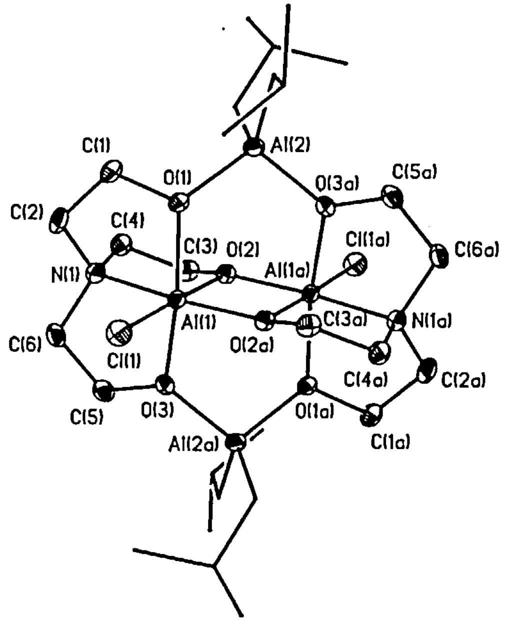


FIGURE 1 A view of the $[(C_4H_9)_2Al\{N(CH_2CH_2O)_3\}Al(Cl)]_2$, I, molecule showing the atom labelling scheme. Thermal ellipsoids show 25% probability levels; hydrogen atoms have been omitted.

TABLE III

Selected bond distances (Å) and angles (deg) for $[(C_4H_9)_2Al\{N(CH_2CH_2O)_3\}Al(Cl)]_2$, I.

Atoms	Distance	Atoms	Distance
Cl(1)-Al(1)	2.243(3)	Al(1)-O(2)	1.916(4)
Al(1)-O(1)	1.910(5)	Al(1)-N(1)	2.003(5)
Al(1)-O(3)	1.931(5)	Al(2)-O(1)	1.858(5)
Al(1)-O(2A)	1.798(4)	Al(2)-O(3a)	1.837(4)
Al(2)-C(11)	1.979(9)	Al(2)-C(7)	1.978(7)
N(1)-C(4)	1.502(8)	O(2)-C(3A)	1.408(7)
N(1)-C(6)	1.495(9)	O(1)-C(1)	1.436(7)
N(1)-C(2)	1.481(9)	O(3)-C(5)	1.437(8)

Atoms	Angle	Atoms	Angle
Cl(1)-Al(1)-O(1)	95.1(2)	Cl(1)-Al(1)-O(2)	177.5(2)
O(1)-Al(1)-O(2)	84.8(2)	Cl(1)-Al(1)-O(3)	95.0(2)
O(1)-Al(1)-O(3)	164.2(2)	O(2)-Al(1)-O(3)	85.7(2)
Cl(1)-Al(1)-N(1)	97.5(2)	O(1)-Al(1)-N(1)	82.6(2)
O(2)-Al(1)-N(1)	84.9(2)	O(3)-Al(1)-N(1)	84.1(2)
C(1)-Al(1)-O(2A)	98.5(1)	O(1)-Al(1)-O(2A)	98.4(2)
O(2)-Al(1)-O(2A)	79.1(2)	O(3)-Al(1)-O(2A)	92.1(2)
N(1)-Al(1)-O(2A)	163.8(2)	O(1)-Al(2)-C(7)	109.2(3)
O(1)-Al(2)-C(11)	109.8(3)	C(7)-Al(2)-C(11)	112.4(3)
O(1)-Al(2)-O(3A)	104.4(2)	C(7)-Al(2)-O(3A)	109.1(3)
C(11)-Al(2)-O(3A)	111.6(3)	Al(1)-O(1)-Al(2)	123.1(2)
Al(1)-O(1)-C(1)	113.2(4)	Al(2)-O(1)-C(1)	117.4(4)
Al(1)-O(2)-C(3)	114.9(4)	Al(1)-O(2)-Al(1A)	100.9(2)
C(3)-O(2)-Al(1A)	138.7(4)	Al(1)-O(3)-C(5)	115.1(4)
Al(1)-O(3)-Al(2A)	121.3(2)	C(5)-O(3)-Al(2A)	122.2(4)
Al(1)-N(1)-C(4)	108.1(4)	Al(1)-N(1)-C(2)	105.4(4)
Al(1)-N(1)-C(6)	105.5(3)	C(2)-N(1)-C(4)	111.1(5)
C(4)-N(1)-C(6)	113.4(5)	C(2)-N(1)-C(6)	112.7(5)
C(18)-N(2)-C(20)	113.1(5)	O(1)-C(1)-C(2)	111.4(5)
N(1)-C(2)-C(1)	109.3(5)	O(2)-C(3)-C(4)	107.1(5)
N(1)-C(4)-C(3)	111.3(4)	O(3)-C(5)-C(6)	109.4(6)
N(1)-C(6)-C(5)	108.6(5)	N(2)-C(20)-C(19)	110.3(6)
Al(2)-C(16)-C(12A)	124.4(16)	Al(4)-C(25)-C(26)	122.0(16)
N(2)-C(18)-C(15)	110.0(5)	Al(4)-C(21)-C(22)	117.3(6)
N(2)-C(20)-C(17)	111.6(6)	Al(4)-C(25A)-C(26A)	130.2(32)

163.8(2), and 177.5(2)°, respectively. thus, the coordination of Al(1) and Al(1a) may be regarded as distorted octahedral.

The literature is replete with organoaluminum compounds containing Al–O bonds characterized by single crystal X-ray diffraction.[8] One may consider three types of Al–O bonds in **I**: bridging Al–O bonds (Al(2)–O(1), Al(2)–O(3a)), core Al–O bonds (Al(1)–O(1), Al(1)–O(2a), Al(1)–O(3)), and Al–O bonds *trans* to the chlorine atoms (Al(1)–O(2), Al(1a)–O(2a)). The two bridging aluminum atoms, Al(2) and Al(2a), have Al–O bond distances of 1.858(5) and 1.837(4) Å, respectively. The core aluminum atoms, Al(1) and Al(1a), have various Al–O bond lengths. The Al–O bond distances

TABLE IV
Final fractional atomic coordinates (× 10^4) for $[(CH_3)Ga.[14]aneN_4]Cl_2$, **II**.

Atom	*x/a*	*y/b*	*z/c*	*U(eq)**
Ga(1)	2994(1)	4731(1)	815(1)	28(1)
Cl(1)	1120(2)	6128(3)	1293(2)	48(1)
Cl(2)	3643(2)	614(3)	1951(3)	66(2)
Cl(3)	−124(9)	4811(9)	5180(8)	60(4)
Cl(4)	1109(6)	5778(8)	4018(6)	69(3)
N(1)	1548(6)	4139(8)	−337(6)	30(3)
N(2)	2693(6)	3376(8)	1791(6)	32(3)
N(3)	3868(7)	5825(8)	2172(6)	34(3)
N(4)	2639(7)	6445(8)	18(6)	38(4)
C(1)	1457(8)	2855(9)	−55(9)	36(4)
C(2)	1649(8)	2819(11)	1145(9)	38(5)
C(3)	2831(9)	3634(11)	2942(8)	46(5)
C(4)	3833(8)	4351(11)	3599(8)	41(4)
C(5)	3778(9)	5677(11)	3247(9)	43(5)
C(6)	3767(10)	7166(11)	1836(9)	47(5)
C(7)	3555(9)	7277(12)	626(9)	51(5)
C(8)	2299(10)	6428(12)	−1193(10)	56(6)
C(9)	1293(10)	5731(12)	−1781(9)	53(5)
C(10)	1388(10)	4345(12)	−1521(9)	49(5)
C(11)	4057(9)	3923(12)	380(9)	48(5)
C(12)	1012(18)	5649(22)	5328(18)	44(10)

* Equivalent isotropic U (× 10^3) defined as one third of the trace of the orthogonalized U_{ij} tensor.

for Al(1)–O(1), Al(1)–O(2a), Al(1)–O(3) are 1.910(5), 1.798(4), 1.931(5) Å, respectively. Importantly, the Al(1)–(O2a) bond distance (1.798(4) Å) is among the shortest Al–O bonds reported. The Al(1)–O(2) bond *trans* to the chlorine atom has a bond distance at 1.916(4) Å. Certainly, steric strain about the core Al atoms contributes to this range of Al–O bond distances. This variation of Al–O bond distances notwithstanding, the values observed in **I** are comparable to other high oxygen content organoaluminum compounds.[9]

It is important to note that triethanolamine has previously been examined by Healy and Barron[10] in the preparation of $[Al(CH_3)_2\{N(CH_2CH_2O)_3\}Al(CH_3)]_2$, **III**. This compound was prepared by the reaction of triethanolamine with trimethylaluminum. The Al–O frameworks of compounds **I** and **III** are identical in that both compounds contain aluminum atoms that are six-coordinate. Other compounds containing six-coordinate aluminum have been prepared in our laboratory. Reaction of diisobutylaluminum hydride and tris(2-aminoethyl)amine (tren), the primary amine analogue of triethanolamine, yielded $[Al(C_4H_9)_2Cl][Al(tren)_2.AlCl]$-$[Al(C_4H_9)]_2$(**IV**).[11] Compound **IV** has an aluminum-nitrogen framework which is similar to the aluminum-oxygen framework of compounds **I** and **III**. In compound **IV**, the formation of an Al–Cl bond, originating from the participation of methylene chloride, was also observed.

The X-ray crystal structure of **II** is shown in Figure 2. Compound **II** consists of a $[(CH_3)Ga.[14]aneN_4]^{+2}$ cation, two chloride anions and one half-occupancy

TABLE V
Selected bond distances (Å) and angles (deg) for $[(CH_3)Ga.[14]aneN_4]Cl_2$, **II.**

Atoms	Distance	Atoms	Distance
Ga(1)–N(1)	2.065(7)	Ga(1)–N(2)	2.092(9)
Ga(1)–N(3)	2.071(8)	Ga(1)–N(4)	2.078(8)
Ga(1)–C(11)	1.982(14)	Cl(3)–C(12)	1.755(28)
Cl(4)–C(12)	1.785(28)	N(1)–C(1)	1.449(13)
N(1)–C(10)	1.497(15)	N(2)–C(2)	1.476(12)
N(2)–C(3)	1.474(14)	N(3)–C(5)	1.476(16)
N(3)–C(6)	1.498(14)	N(4)–C(7)	1.494(14)
N(4)–C(8)	1.467(15)	C(1)–C(2)	1.492(16)
C(3)–C(4)	1.517(15)	C(4)–C(5)	1.491(16)
C(6)–C(7)	1.501(17)	C(8)–C(9)	1.495(17)

Atoms	Angle	Atoms	Angle
N(1)–Ga(1)–N(2)	82.0(3)	N(1)–Ga(1)–N(3)	149.7(4)
N(2)–Ga(1)–N(3)	93.4(3)	N(1)–Ga(1)–N(4)	86.6(3)
N(2)–Ga(1)–N(4)	149.5(4)	N(3)–Ga(1)–N(4)	82.4(3)
N(1)–Ga(1)–C(11)	105.5(4)	N(2)–Ga(1)–C(11)	103.1(5)
N(3)–Ga(1)–C(11)	104.7(4)	N(4)–Ga(1)–C(11)	107.2(5)
Ga(1)–N(1)–C(1)	105.4(5)	Ga(1)–N(1)–C(10)	114.2(7)
C(1)–N(1)–C(10)	114.5(8)	Ga(1)–N(2)–C(2)	108.8(6)
Ga(1)–N(2)–C(3)	121.5(7)	C(2)–N(2)–C(3)	111.0(9)
Ga(1)–N(3)–C(5)	121.1(7)	Ga(1)–N(3)–C(6)	109.9(5)
C(5)–N(3)–C(6)	110.6(9)	Ga(1)–N(4)–C(7)	106.5(6)
Ga(1)–N(4)–C(8)	116.4(7)	C(7)–N(4)–C(8)	114.8(10)
N(1)–C(1)–C(2)	107.3(8)	N(2)–C(2)–C(1)	108.2(10)
N(2)–C(3)–C(4)	113.0(11)	C(3)–C(4)–C(5)	112.9(8)
N(3)–C(5)–C(4)	112.8(10)	N(3)–C(6)–C(7)	110.1(10)
N(4)–C(7)–C(6)	106.3(10)	N(4)–C(8)–C(9)	113.0(12)
C(8)–C(9)–C(10)	113.4(9)	N(1)–C(10)–C(9)	110.0(10)
Cl(3)–C(12)–Cl(4)	110.3(11)		

methylene chloride solvent molecule. The four nitrogen atoms of $[14]aneN_4$ are coplanar (mean deviation from plane of 0.0036 Å). The gallium atom of the methylgallium unit, Ga(1), resides 0.540 Å out of the N_4 plane. The chloride anions appear to be hydrogen bonded to the aza-hydrogen atoms with Cl···N distances ranging from 3.172(7) to 3.247(7) Å. The chloride anion Cl(1) bridges atoms N(1) and N(4). The other chloride ion, Cl(2), interacts with N(2) of one cation and N(3) of a cation related by a 2_1 screw-axis, forming an infinite hydrogen-bonded chain (Figure 3). The bridging chloride Cl(1) is in contact with the gallium atom Ga(1) (Cl(1)–Ga(1) = 3.272(5) Å). Although this contact could be a coincidental result of the NH···Cl hydrogen bonding, it does complete a distorted octahedral coordination sphere about the gallium atom. The Ga–N bond distances in compound **II**, ranging from 2.065(7) to 2.092(9) Å, are comparable to those reported for other organogallium compounds.[12]

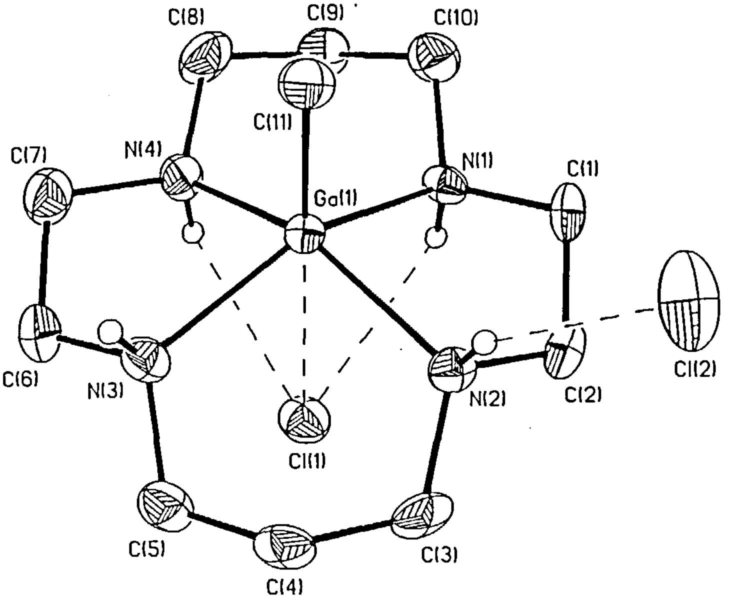


FIGURE 2 A view of the $[(CH_3)Ga.[14]aneN_4]Cl_2$, **II**, *molecule showing the atom labelling scheme.* Thermal ellipsoids show 35% probability levels; hydrogen atoms have been omitted.

The conformation of $[14]aneN_4$ is worthy of note. Severe distortion of $[14]aneN_4$ has been observed in a number of organoaluminum and organogallium derivatives prepared in this laboratory.[13] However, in compound **II** the conformation of $[14]aneN_4$ is essentially in the same endodentate conformation as observed for the uncomplexed macrocycle.[14]

The mechanism leading to the formation of **II** is believed to also involve the solvent participation of methylene chloride. It is reasonable to consider Ga–R/N–H condensation (and alkane elimination) to yield $[(CH_3)Ga.[14]aneN_4]$ in the first step (methylene chloride was added to the flask 24 hours after the reaction started). $[(CH_3)Ga.[14]aneN_4]$ then reacted with 2 equivalents of HCl, possibly generated from a Friedel-Crafts reaction, producing compound **II** (equation (*1*)). The abstraction of HCl has been reported in reactions involving aromatic solvent, CH_2Cl_2 and $AlCl_3$ as a catalyst.[15] In the case of compound **II**, excess trimethylgallium may serve as the Lewis acid catalyst.

$$[(CH_3)Ga\cdot[14]aneN_4]+2HCl \rightarrow [(CH_3)Ga\cdot[14]aneN_4]Cl_2 \qquad (1)$$

The participation of solvent in reactions between Lewis bases and aluminum and gallium alkyls has gained our attention. In addition to compounds **I**, **II**, and **IV**, we have also isolated other organoaluminum compounds containing Al–Cl bond originating from methylene chloride.[11] Future work will further explore the effect of solvents on group 13 coordination chemistry.

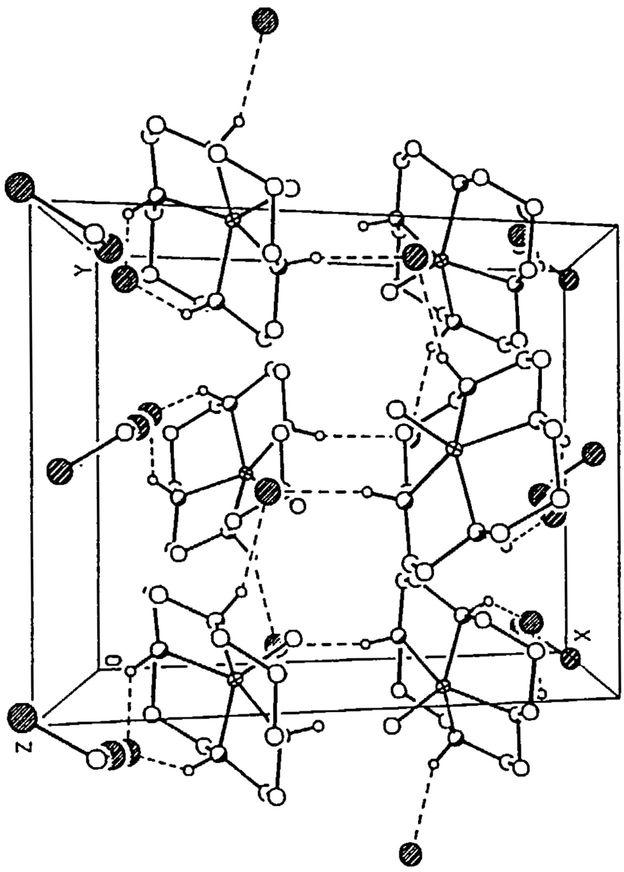


FIGURE 3 Crystal packing diagram of [(CH$_3$)Ga.[14]aneN$_4$]Cl$_2$, II, viewed along *c*.

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SUPPLEMENTARY MATERIAL

Summary of data collection and refinement, molecular plots, tables of bond distances and angles, final fractional coordinates, thermal parameters and a listing of observed and calculated structure factors are available from G.H.R.

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