

MONOMERIC CHELATED AMIDES OF ALUMINUM AND GALLIUM: VOLATILE, MISCIBLE LIQUID PRECURSORS FOR CVD

SEÁN T. BARRY, ROY G. GORDON and VALERIE A. WAGNER
Harvard University Chemical Laboratories
Cambridge, MA 02138

ABSTRACT

New precursors were developed for the chemical vapor deposition (CVD) of aluminum nitride (AlN) and gallium nitride (GaN) at low temperatures. Synthetic methods for the new materials will be reported, along with their analyses and spectral characterization. The precursors are volatile (180 mTorr at 45-55 °C), low-viscosity (10 centipoise) liquids, so they are more convenient as vapor sources than previously available solid sources. They are thermally stable to temperatures well above their vaporization temperatures, so their vaporization is highly reproducible and leaves no residue. Unlike previously available liquid precursors, they are not pyrophoric, so they are safer to handle. AlN films formed by reaction with ammonia at around 200 °C are amorphous, transparent insulators that are good barriers to diffusion of water, oxygen, and other materials.

INTRODUCTION

The nitrides of aluminum and gallium have been deposited from a variety of metal-containing sources. Vapors of the metal alkyls react with ammonia at elevated temperatures (typically over 1000 °C) to form films of the metal nitrides.¹ These metal alkyls are spontaneously flammable in air, and the handling and shipping of these pyrophoric liquids presents serious safety hazards. The dialkylamides of aluminum² and gallium³ allow CVD of the metal nitrides at much lower temperatures, 200 to 400 °C, and are much safer to handle because they are not pyrophoric. However, aluminum and gallium dimethylamides are solids, so they are less convenient to handle and vaporize than liquid precursors. The purpose of this paper is to introduce non-pyrophoric liquid precursors for CVD of AlN and GaN. These materials have the general formula shown in Figure 1. The chelating amide ligand is designed to keep them monomeric. This increases their volatility compared to the dimeric dimethylamides, and helps to keep them liquid, rather than solid.

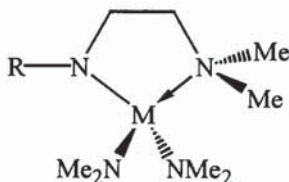


Figure 1. The general formula of a series of group 13 chelated amides designed to be low viscosity, monomeric liquids. M = Al or Ga and R = Me or Et.

Recently, the compound (Me₂NCH₂CH₂NMe)Al(NMe₂)₂ was synthesized.⁴ Unfortunately, there was no physical characterization nor reactivity reported for this material, and its extent of

oligomerization was not addressed. This work will expand what is known about this compound, as well as exploring other diamine ligands and examining similar reactivity for gallium.

EXPERIMENTAL AND RESULTS

All syntheses were performed using standard Schlenk techniques. All NMR spectra were taken on either a Bruker AM 500 MHz or a Bruker AM 300 MHz NMR spectrometer. Diethylether was dried over Na/K alloy and used freshly distilled. Both diamines were purchased from Aldrich Chemical Company and distilled before use. The hexakis(dimethylamido)digallium was made according to the seminal literature preparation⁵; the hexakis(dimethylamido)dialuminum was a gift from Aldrich Chemical Company.

Transamination from the starting material $[M(NMe_2)_3]_2$ (where M = Al, Ga) proved to be facile. The reaction occurred at room temperature under stirring for both $[Al(NMe_2)_3]_2$ and $[Ga(NMe_2)_3]_2$.



The syntheses were performed neat, with the diamine initially behaving as the solvent and the liquid product acting as the solvent towards the end of the reaction.

Synthesis of $Al(N(CH_3)CH_2CH_2N(CH_3)_2)(N(CH_3)_2)_2$ (1).

In a 100-mL flask, $[Al(N(CH_3)_2)_3]_2$ (2.0 g, 12.6 mmol) and $(CH_3)_2NCH_2CH_2NH(CH_3)$ (1.63 mL, 12.6 mmol) were mixed, and the clear, slightly orange solution was stirred overnight. Volatile materials were removed *in vacuo*, and clear, colorless **1** (2.54 g, 88 % yield) was distilled out at 65–70 °C at 300 mTorr with the distillation condenser just above ambient temperature. C: 51.76% found, 52.14% calc., H: 11.82% found, 11.92% calc., N: 24.32% found, 23.92% calc. ¹H NMR: (2.85 ppm, singlet, 12H), (2.70 ppm, double doublet, 2H), (2.15 ppm, double doublet, 2H), (2.03 ppm, singlet, 3H), (1.75 ppm, singlet, 6H)

When N,N,N'-trimethylethylenediamine (H3meda) was added to solid $[Al(NMe_2)_3]_2$ at room temperature, a slightly orange, clear liquid formed immediately with effervescence. After stirring over night at room temperature, **1** was distilled off in high yield between 65–70 °C. It was a clear, colorless liquid that froze around 26 °C (Table I). Compound **1** crystallized from the melt, and a single crystal X-ray diffraction study revealed the material to be a monomer with two molecules in the unit cell. Of the nitrogen-aluminum bonds, three were within the range 1.805–1.810 Å, which is expected for a covalent bond. The dative bond from the tertiary amine in the diamine was longer (2.036 Å).

Compound **1** was found to be a monomer in solution by using the melting point depression of *p*-xylene. The molecular complexity that is reported in Table I is the ratio of the experimental molecular weight divided by the calculated molecular weight of the monomer.

Table I. Physical data for liquid aluminum and gallium compounds. Note compound 1 (*) is a solid at room temperature and melts around 26°C.

Compound	Observed T _{bp} T (°C)/P (mTorr)	Corrected T _{bp} (°C)	Molecular Complexity	Viscosity (centipoise)
Al(3meda)(NMe ₂) ₂ (1)	65-70/300	250-255	1.04	10.22*
Al(dmeeda)(NMe ₂) ₂ (2)	65-70 /300	250-255	1.10	12.92
Ga(3meda)(NMe ₂) ₂ (3)	48-55/180	247-254	1.33	16.60
Ga(dmeeda)(NMe ₂) ₂ (4)	65-70/180	260-265	1.04	10.08

Synthesis of Al(N(CH₂CH₃)CH₂CH₂N(CH₃)₂)(N(CH₃)₂)₂ (2).

In a 100-mL flask, [Al(N(CH₃)₂)₃]₂ (2.0 g, 12.6 mmol) and (CH₃)₂NCH₂CH₂NH(CH₂CH₃) (2.0 mL, 13.2 mmol) were mixed, and the clear, slightly orange solution was stirred overnight. Volatile materials were removed *in vacuo*, and clear, colorless 2 (2.69 g, 93 % yield) was distilled out at 65-70 °C at 300 mTorr. C: 50.17% found, 49.98% calc., H: 11.62% found, 11.65% calc., N: 24.64% found, 25.90% calc. ¹H NMR: (3.04 ppm, quartet, 2H), (2.82 ppm, singlet, 12H), (2.75 ppm, double doublet, 2H), (2.15 ppm, double doublet, 2H), (1.78 ppm, singlet, 6 ppm), (1.32 ppm, triplet, 3H)

When N,N-dimethyl-N'-ethylethylenediamine (Hdmeeda) was added to solid [Al(NMe₂)₃]₂, a clear orange liquid immediately formed. Effervescence was not obvious, but after stirring overnight Al(dmeeda)(NMe₂)₂ (2) distilled off at 65-70 °C at 300 mTorr as a clear, colorless liquid (Table 1). Compound 2 was also a monomer in *p*-xylene.

Synthesis of Ga(N(CH₃)CH₂CH₂N(CH₃)₂)(N(CH₃)₂)₂ (3).

In a 100-mL flask, GaCl₃ (5.0 g, 28.4 mmol) was cooled to 0 °C, and 50 mL of diethylether was slowly added. In a 200-mL flask, LiN(CH₃)₂ (4.34 g, 85.1 mmol) was suspended in 50 mL of diethylether and cooled to 0 °C. The GaCl₃ solution was added by cannula to the LiN(CH₃)₂ suspension with immediate precipitation. The mixture was refluxed at 45 °C over night. The solids were filtered off, and (CH₃)₂NCH₂CH₂NH(CH₃) (3.70 mL, 28.4 mmol) was added by syringe. The solution was refluxed at 45 °C for 3 hours and the volatile materials were removed *in vacuo*. Clear, colorless 3 (5.08 g, 81% yield) was distilled off at 65-70 °C at 180 mTorr. C: 41.73% found, 41.35% calc., H: 9.72% found, 9.93% calc., N: 21.63% found, 20.24% calc. ¹H NMR: (3.03 ppm, double doublet, 2H), (2.84 ppm, singlet, 12H), (2.50 ppm, double doublet, 2H), (2.21 ppm, singlet, 3H), (2.17 ppm, singlet, 6H)

When H3meda was added to [Ga(NMe₂)₃]₂, effervescence was immediate, and a slightly yellow, clear liquid formed. After stirring overnight, clear colorless 3 distilled off at 48-55 °C at 180 mTorr. A melting point depression experiment in *p*-xylene showed 3 to have a molecular complexity of 1.33, suggesting a monomer/dimer equilibrium. This equilibrium does not seem to affect the distillation temperature, which was similar to the rest of the reported compounds. However, the higher viscosity of 3 is possibly due to this monomer/dimer exchange (Table I).

Synthesis of Ga(N(CH₂CH₃)CH₂CH₂N(CH₃)₂)(N(CH₃)₂)₂ (4).

In a 100-mL flask, [Ga(NCH₃)₂]₂ (2.29 g, 11.3 mmol) and (CH₃)₂NCH₂CH₂NH(CH₂CH₃) (1.8 mL, 11.4 mmol) were mixed. The clear, yellow solution was allowed to stir overnight. Volatile materials were removed *in vacuo*, and clear, colorless **4** (2.39 g, 77% yield) distilled off at 48-55 °C at 180 mTorr. C: 44.27% found, 43.98% calc., H: 10.49% found, 9.97% calc., N: 20.89% found, 20.52% calc. ¹H NMR: (3.05 ppm, multiplet, 2H), (2.94 ppm, triplet, 2H), (2.84 ppm, singlet, 12H), (2.51 ppm, double doublet, 2H), (2.19 ppm, singlet, 6H), (1.25 ppm, triplet, 3H)

This monomer/dimer exchange does not seem to occur in Ga(dmeeda)(NMe₂)₂ (**4**). After Hdmeeda and [Ga(NMe₂)₃]₂ were subjected to the aforementioned reaction conditions, clear, colorless **4** distilled off at 65-70 °C. It was a monomer in *p*-xylene, unlike compound **3**.

Thermal decomposition studies.

Thermolyses of these compounds were performed in sealed heavy-walled NMR tubes. The solvent used was d₁₂-mesitylene with some mesitylene as an internal standard. The decomposition was followed by the loss of an isolated signal in the ¹H NMR spectrum (a 1.94 ppm singlet for compounds **1** and **3**; a 1.34 ppm multiplet in the case of **2** and **4**).

The decomposition of compound **1** occurred at 275 °C with a half-life of 29 minutes. The loss of the peak followed a linear path over the time frame measured. In contrast, compound **2** showed no decomposition at this temperature and only started to decompose at 300 °C with a half-life of 10.5 minutes. Both of these decompositions produced orange, soluble byproducts. Peaks for these byproducts were evident in the NMR, but were too numerous to offer any information about their structure.

Decomposition for **3** occurred at 212 °C with a half-life of 50 minutes. During the course of the thermolysis, a gray insoluble material formed, and the solution turned orange. Again, the soluble byproducts were uncharacterizable. Compound **4** decomposed at the same temperature with a half-life of 37 minutes. A gray precipitate formed in the course of this thermolysis as well.

Reactivity with ammonia

All four compounds showed reactivity with ammonia at room temperature. In a typical reaction, 0.5g of material was taken up in 5 mL of dry ether in an inert atmosphere. Ammonia gas was bubbled into the solution and an intractable white solid precipitated immediately. Characterization of the white solid by IR showed a strong absorption in the N-H stretching region in each case.

CVD of aluminum nitride from **2** and ammonia.

Thin films were grown by atmospheric pressure chemical vapor deposition (APCVD). Compound **2** was diluted with mesitylene (2.08 g of **2** in 3.47 g mesitylene) and vaporized by ultrasonic nebulization. The high-frequency (1.4 MHz) ultrasonic system created a cloud of tiny droplets (approximately 20-30 microns in diameter) in a reproducible and well-controlled manner.⁶ The resulting fog was carried by a low flow of nitrogen (0.5 L/min, filtered by an

oxygen scavenger) into a glass reaction tube surrounded by a tube furnace at 200 °C. Ammonia diluted by nitrogen in a 1:1 molar ratio was also introduced into the reaction tube. This mixture was used to purge the CVD system for 3 h prior to deposition. The precursor concentration in the deposition gas stream was 0.41 mol%, the ammonia concentration was 14 mol%, and the total flow rate was 0.70 L/min. Films were deposited on silicon substrates resting on the bottom of the glass tube. The deposition occurred over 6 minutes, and then the furnace was allowed to cool to room temperature under a flow of N₂/NH₃. Rutherford Backscattering (RBS) was used to determine the elemental composition of the films.

DISCUSSION

In this system, transamination occurs at room temperature to produce volatile liquid mixed amides of aluminum and gallium. All of the compounds have viscosities below 20 centipoise at room temperature, which makes them very easy to handle in a CVD reactor. Also, their low boiling points allow for fast vaporization and easy transport to the substrate.

The relatively low boiling points and viscosities of these materials suggest that intermolecular interaction is low. With the exception of compound **3**, these compounds are monomers in a non-coordinating solvent. This is due to bidentate coordination of the diamine ligand. This allows for the coordinative saturation of the metal center. Indeed, the X-ray diffraction study of **1** demonstrates this (Figure 2).

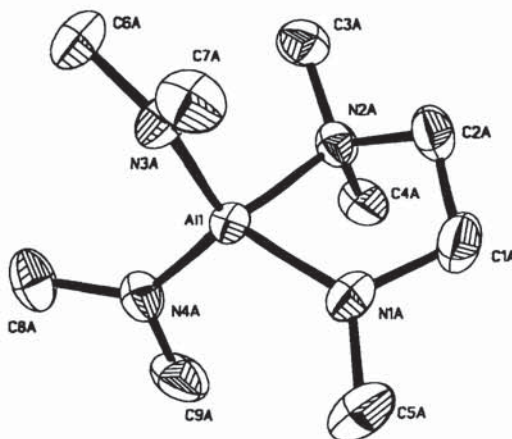


Figure 2. The molecular structure of **1** determined by X-ray diffraction from a single crystal. The thermal ellipsoids represent 50% probability.

Both dimethylamido moieties are planar, with the sum of the angles with nitrogen at the vertex totaling 360.0° and 359.6°. Planarity (359.0°) was also found in the amido end of the bidentate ligand. This is likely an average over several different orientations of the more usual umbrella structure.

The amino end of the bidentate ligand was found to be a distorted tetrahedron, with the Al-N-C (ring) angle being narrowed at the expense of the other two Al-N-C vertices. The dihedral

angle in the N-C-C-N moiety was 40.23° , which approaches a typical dihedral angle in an alkane ring (55°). The N-Al-N ring angle is 87° , which is surprisingly small for the distorted tetrahedron around aluminum. Finally, the angles between the amido nitrogen of the bidentate ligand and the nitrogen of the dimethylamido moieties were all between 115 - 116° . This suggests that the ring is strained by the dihedral twist of the ethylene bridge, and this is pulling the amido nitrogen closer to the amino nitrogen of the bidentate ligand and forcing a distortion of the aluminum tetrahedron.

In the case of compound **3**, the molecular weight data and NMR spectrum suggest a monomer/dimer equilibrium. This is likely a steric effect, with the extra bulk of the ethyl group in **4** hindering the metal center just enough to prevent dimerization. Barron *et al.* have done extensive work on bidentate ligands with different heteroatoms and have found that the strength of the metal-nitrogen bond and tetrahedral geometry of the coordinated amine promote dissociation from a 5-coordinate metal center to a monomer as steric bulk increases.⁷

All the compounds synthesized were found to be miscible with each other, as well as with nonpolar, aprotic organic solvents such as hydrocarbons.

Deposition of a thin film of aluminum nitride from compound **2** was possible at 200°C in a flow of ammonia carried by nitrogen. The film was entirely aluminum oxide close to the introduction of precursor (near end) and became predominantly aluminum nitride at the other end of the substrate (far end), as characterized by Rutherford Backscattering (RBS). This was likely due to an incidental oxygen source being introduced by a leak in the system or by the gas stream. Since the gas delivery system was equipped with an O_2 scavenger, it is likely that the oxygen source was water. At the near end of the film, **2** reacted preferentially with water to form aluminum oxide, depleting the gas stream of water. At the far end of the film, **2** reacted with ammonia to form aluminum nitride. Since reactivity with NH_3 was seen to occur easily at room temperature and compound **2** showed no thermal reactivity until 300°C , ammonia was the obvious nitrogen source for the aluminum nitride film. This reactivity with ammonia is well-documented in the literature.⁸

A more detailed look at the RBS spectrum of the aluminum nitride reveals some interesting features (Figure 3). Appearance of a sharp oxygen peak demonstrates that there was a veneer of Al_2O_3 on the surface of the aluminum nitride. This 500 \AA thick layer could have been caused by two factors. If the film was porous enough to react with atmospheric water or dioxygen, this layer could have formed upon exposing the film to air. The Al_2O_3 then passivated the surface to prevent reaction of the rest of the aluminum nitride layer. Another possible explanation is that the Al_2O_3 surface layer formed as the reaction conditions at the end of the deposition changed. That is to say, as the furnace cooled from 200°C to room temperature, reaction with incidental water slowed at the near end of the film, and subsequently water became available for reaction at the far end of the film.

The RBS analysis also showed an aluminum nitride film with a thickness of 7000 \AA . Interestingly, the simulation gave an Al:N ratio of 1:2.2. This overabundance of nitrogen could be due to the presence of hydrogen (undetectable by RBS) in the film from incomplete reaction with the ammonia.

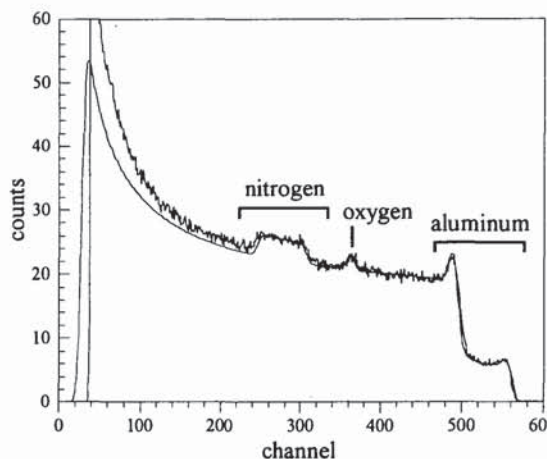


Figure 3: RBS spectrum for an Aluminum nitride film deposited using $\text{Al}(\text{dmeeda})(\text{NMe}_2)_2$ (2) and NH_3 at 200°C . The thin, smooth line is a calculated fit to the spectrum.

CONCLUSIONS

Volatile liquid compounds of aluminum and gallium were synthesized, and their physical properties measured. These materials are low viscosity liquids that distill easily under vacuum. They are much safer to handle than the metal alkyls and react at much lower temperatures. These materials are thermally stable up to 200°C and react readily with ammonia even at room temperature. They are highly suitable for CVD of aluminum nitride, gallium nitride, or their alloys, which has been demonstrated by synthesizing an aluminum nitride film.

ACKNOWLEDGMENT

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REFERENCES

1. See, for example, C.-M. Zetterling, M. Ostling, K. Wongchotigul, M. G. Spencer, X. Tang, C. I. Harris, N. Nordell and S. S. Wong, *J. Appl. Phys.* **82**, 2990 (1997).
2. R. G. Gordon, U. Riaz and D. M. Hoffman, *J. Mater. Res.* **7**, 1679 (1992).
3. R. G. Gordon, D. M. Hoffman and U. Riaz, (*Mat. Res. Soc. Symp. Proc.* **204**, Pittsburgh, PA, 1991) p. 95.
4. B. A Vaartstra, US Patent 5,908,947 (1999).
5. H. Nöth,; P. Konrad, , *Z. Naturforsch.*, **30b**, 681 (1975).
6. R. G. Gordon, F. Chen, N. J DiCeglie, Jr., A. Kenigsberg, X. Liu, D. J. Teff and J. Thornton, *Mat. Re. Soc. Symp. Proc.* **495**, pp. 63 (1998).
- 7 C. N. McMahon, J. A. Francis, S. G. Bott, A. R. Barron, *J Chem. Soc., Dalton Trans.*, 67 (1999).
8. for an example, see: J. F. Janik, and R. L. Wells, *Chem. Mater.*, **10**, 1613-1622 (1998).