

## Poly(imidogallane): Synthesis of a Crystalline 2-D Network Solid and Its Pyrolysis To Form Nanocrystalline Gallium Nitride in Supercritical Ammonia

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The growing interest in nanocrystalline GaN has been enhanced by the recent development of suitable synthetic methods.<sup>1–10</sup> Unfortunately, these methods offer minimal control over particle size and dispersion. Cyclotrigallazane, **1**, a molecular solid that exhibits intermolecular, so-called unconventional hydrogen bonds,<sup>11</sup> dehydrogenates in the solid state to form nanocrystalline gallium nitride. While searching for a more controlled solution-based route to GaN, we isolated a polymeric intermediate in the conversion of cyclotrigallazane to GaN in supercritical NH<sub>3</sub>; a solvent known to be useful for the preparation of solid-state compounds.<sup>12–14</sup>

Cyclotrigallazane, [H<sub>2</sub>GaNH<sub>2</sub>]<sub>3</sub>, was prepared by the direct reaction of GaH<sub>3</sub>(NMe<sub>3</sub>) with NH<sub>3</sub> at –33 °C<sup>11</sup> and was found to redissolve in liquid ammonia. As the only other solvents reported to dissolve [H<sub>2</sub>GaNH<sub>2</sub>]<sub>3</sub> also contained donor groups,<sup>15</sup> we suspected that ring cleavage and donor coordination were responsible for the enhanced solubility. To gain insight into the degree of association of cyclotrigallazane in solution, a sample of [H<sub>2</sub>GaNH<sub>2</sub>]<sub>3</sub> was dissolved in liquid ND<sub>3</sub>. Following removal of excess ND<sub>3</sub>, the infrared spectrum of the white crystalline solid (Figure 1) was consistent with >95% conversion to [H<sub>2</sub>GaND<sub>2</sub>]<sub>3</sub> (**2**).<sup>11</sup> The H/D exchange most likely occurred directly on the donor–acceptor complex H<sub>2</sub>Ga(NH)<sub>2</sub>(ND<sub>3</sub>) (Scheme 1), as proposed in related transaminations.<sup>7</sup>

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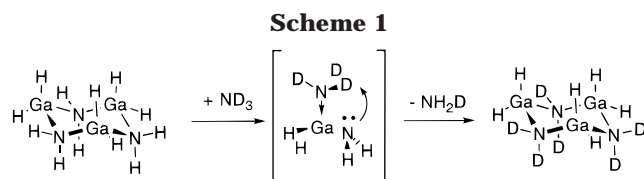
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Heating a solution of [H<sub>2</sub>GaNH<sub>2</sub>]<sub>3</sub> in NH<sub>3</sub> to 150 °C for 30 min in an autoclave resulted in complete conversion to a solid material that was isolated following evaporation of the NH<sub>3</sub> and washed with dimethyl sulfoxide (DMSO), leaving an off-white product. The new species was involatile and insoluble in all solvents except for strong mineral acids with which it reacted with gas evolution. It was relatively stable with regard to atmospheric oxygen and moisture. Changes in reaction time from 10 min to 1.5 h or reactor pressure from 17 to 71 atm had no effect on the outcome. Lowering the reaction temperature (100 °C) and time (5 min) resulted in incomplete conversion, and use of THF as the solvent, in place of liquid ammonia, led to gray decomposition products.

Elemental analysis yielded H:N:Ga ratios of 2.06:1.03:1. Together these elements accounted for 95.4% of the mass of the samples analyzed by ICP-MS for Ga and combustion methods for C, H, and N. Carbon, presumably from residual DMSO, accounted for 1.13%, and we suspect the remainder is due to oxygen and sulfur. The DMSO rinse was necessary to remove contaminants resulting from autoclave O-ring (Viton) degradation. Use of poly(ethylenepropylene) O-rings eliminated the need for the DMSO rinse and lowered the carbon contamination to 0.84%, but the resulting powder contained excess nitrogen and hydrogen. Calculated and experimental values agree for a formula containing 10% residual ammonia, HGaNH·0.1NH<sub>3</sub>. These results are most consistent with the formulation of the product as the polymeric hydridogallium imide, [HGaNH]<sub>n</sub>, **3**.

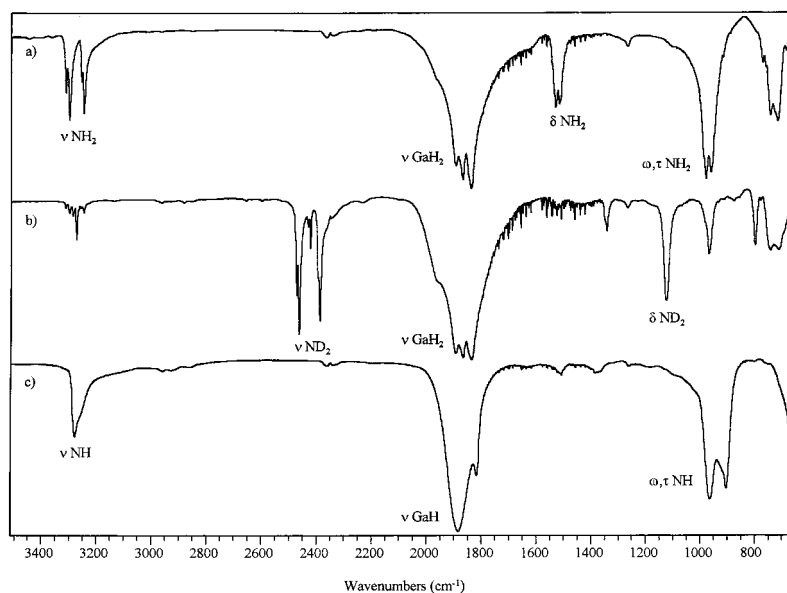
The IR spectrum of **3**, also shown in Figure 1, is simplified compared to that of **1**. The single peak at 3279 cm<sup>-1</sup> is consistent with the presence of an imide (NH). The Ga–H stretch appears as a strong, broad peak at 1885 cm<sup>-1</sup> and a sharper, less intense band at 1817 cm<sup>-1</sup>. The peaks at 964 and 903 cm<sup>-1</sup> are attributed to the wagging motion of the N–H. Notably absent is any peak in the region around 1510 cm<sup>-1</sup>, due to the scissoring vibration of NH<sub>2</sub> groups.

The as-prepared samples of [HGaNH]<sub>n</sub> were found to be crystalline by X-ray powder diffraction and exhibited a coherent length of approximately 15 nm, as estimated by line broadening (Figure 2). While the small number of reflections precluded an unambiguous assignment of the crystal system, the five distinct reflections were indexed to a hexagonal unit cell.

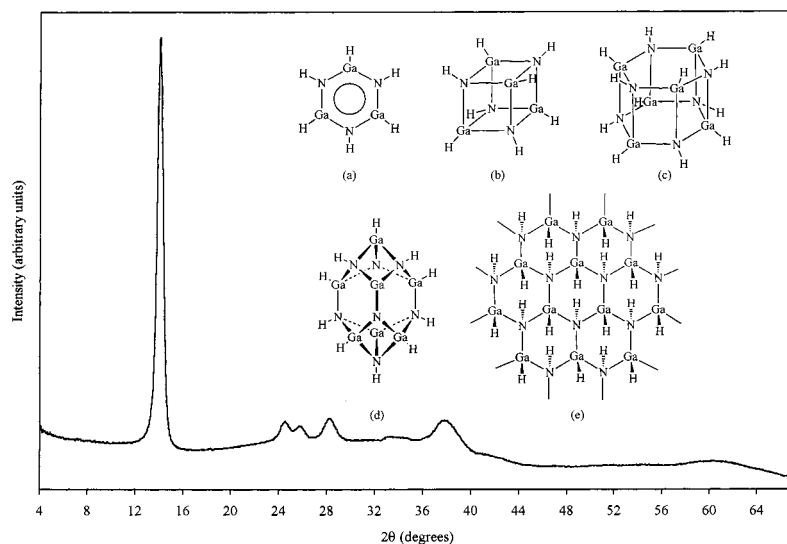
Transmission electron microscopy was conducted by sprinkling the powder over lacy carbon films supported on Cu mesh grids. Particles overhanging the carbon support were used for analysis. Despite use of a liquid

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**Figure 1.** Infrared spectra (KBr pellets) of (a)  $[\text{H}_2\text{GaNH}_2]_3$ , (b)  $[\text{H}_2\text{GaND}_2]_3$ , and (c)  $[\text{HGaNH}]_n$ . Spectrum b indicates the presence of small amounts (approximately 5%) of  $[\text{H}_2\text{GaNH}_2]_3$  and  $[\text{H}_2\text{GaN}(\text{H})\text{D}]_3$ .



**Figure 2.** X-ray powder diffraction pattern for  $[\text{HGaNH}]_n$ , **3**. Possible structures having the appropriate formula. Structure e is most consistent with the properties of **3**.

nitrogen cooled sample stage, the electron beam degraded the samples of **3**, as evidenced by the rapid decay of the diffraction patterns. Bright-field images of the particles show a broadly tabular morphology (Figure 3). The sharp diffraction rings frequently showed strong intensity only over small arcs, rather than being uniformly intense around the whole ring. A few samples (e.g. Figure 3) did show complete rings, with intensity strongly peaked every  $60^\circ$  around the rings. Within the rings there is a streaking of the diffraction spots around the ring, which suggests that within the platelets there are regions which are rotationally misaligned. There is also an appreciable intensity peak corresponding to a rotation of  $90^\circ$  within the plane. These observations suggest that the particles are planar agglomerations, with most of the particles oriented with the basal plane normal to the electron beam (to give complete rings) or slightly off normal (to give the arc patterns). The particles are aligned reasonably well within the layer,

with a small fraction aligned  $90^\circ$  out of phase. The intense peaks can be indexed as a hexagonal (or pseudohexagonal) lattice with a plane spacing of  $6.4 \text{ \AA}$  and a unit cell dimension within the plane of  $7.5 \text{ \AA}$ , which is entirely consistent with the X-ray data. No data could be determined for the unit-cell dimensions normal to the plane.

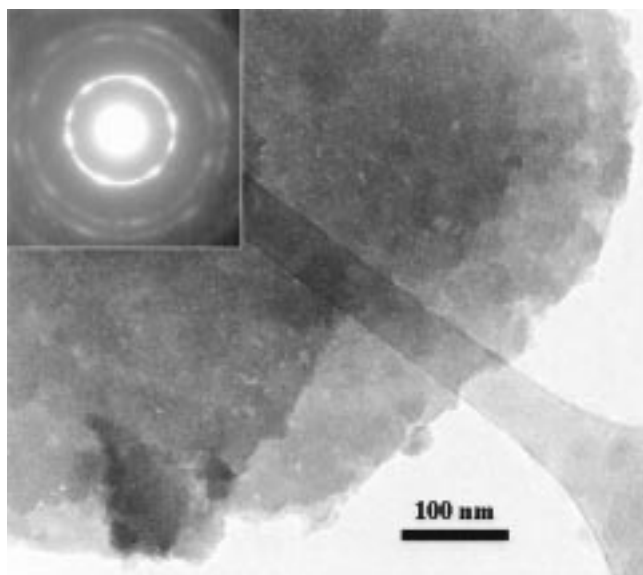
Figure 2 shows possible structures of molecular and solid-state compounds having the formula  $[\text{HGaNH}]_n$ . The clusters drawn in this figure (2a–e) are based upon related, structurally characterized organoaluminum and gallium imides.<sup>16–24</sup> Although none of these can be

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**Figure 3.** TEM and electron diffraction (insert) of poly(imidogallane), **3**. The tabular morphology is evident by the characteristic image density present over large regions of the particle, which is comprised of many small crystallites (not individually visible).

eliminated from consideration, we suggest that the two-dimensional solid state network is more consistent with the solubility, volatility, and electron microscopy. The solid would be composed of stacked covalently bonded layers (such as that shown in Figure 3e). It is possible to envision a crystallographic 3-fold axis perpendicular to the layers which would be consistent with the electron and X-ray diffraction. There is precedent for forming crystalline polymeric precursors to solid-state materials. Poly(borazylene), which contains linked borazine rings, exhibits an X-ray diffraction pattern similar to those

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observed for turbostratic boron nitride.<sup>25</sup> Reports of  $[\text{HAlNH}]_n$  have not suggested any evidence of a crystalline structure.<sup>24</sup>

Thermolysis of **3** in the solid state for 4 h at 600 °C under a flow of  $\text{N}_2$  produced pale yellow, nanocrystalline GaN powder. The nanocrystals were shown by X-ray powder diffraction to consist of a similar, disordered mixture of cubic and hexagonal stacking planes as found in the thermolysis of  $[\text{H}_2\text{GaNH}_2]_3$ ;<sup>2</sup> however, the intensities of the 100 and 101 reflections suggest that the hexagonal layers outnumber the cubic layers. The coherent length of the GaN powders produced from **3** was 5 nm, and the photoluminescence (PL) spectrum of the GaN produced from **3** using an excitation wavelength of 310 nm exhibited an emission peak at 420 nm. Although this is lower in energy than expected on the basis of the band gap of 3.4 eV, the spectrum was similar to that found in other samples of nanocrystalline GaN.<sup>9</sup> Treating **3** for 24 h at 750 °C had little effect on the X-ray diffraction pattern and PL spectrum of the isolated GaN powder.

Extending the original reaction of **1** in ammonia at 150 °C to 5 h results in complete conversion to nanocrystalline GaN (coherent length = 3 nm). Poly(imidogallane), whose formation is complete within 30 min, is apparently an intermediate in this reaction. While the above results suggest **1** dissociates into monomers in liquid  $\text{NH}_3$ , it is less likely that such a reaction would be important for **3**. Unlike the solid-state pyrolysis, extending the reaction time of **1** in supercritical ammonia does result in an increase in the coherent length of the nanocrystals. Details of these and related studies will be described in future publications.

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