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Introduction

Dimethylgallium azide (Me_2GaN_3) and other organogallium azide compounds have attracted recent attention as potential single source precursors for the Chemical Vapor Deposition (CVD) of GaN semiconductor films.[1−7] Gallium nitride is important for applications in near-UV solid-state devices such as high brightness blue LEDs and lasers. As part of our interest in the application of single source precursors for laser-assisted CVD,[8−11] we investigated the excited-state properties of Me_2GaN_3.

Solid-state Raman and Infrared studies reported that the molecule consists of trimeric subunits.[12,13] However, a recent X-ray crystallographic structure shows that dimethylgallium azide is a polymer in the solid state containing low molecular symmetry monomeric subunits.[1]

During the course of our studies of Me_2GaN_3, we observed luminescence from both the solid and from solutions. Emission spectra from a few metal azido complexes have been reported,[14−18] but luminescence from organogallium compounds is not known. In this Note, we report the luminescence, excitation, and absorption spectra of Me_2GaN_3 as the polycrystalline solid and in frozen glasses and solution. Surprisingly, the luminescence spectra from the solid and solution are very similar. Raman vibrational spectra show that the species in the solid and in solution are also very similar. The spectra, the nature of the species in solution, and the assignment of the lowest energy excited state are discussed.

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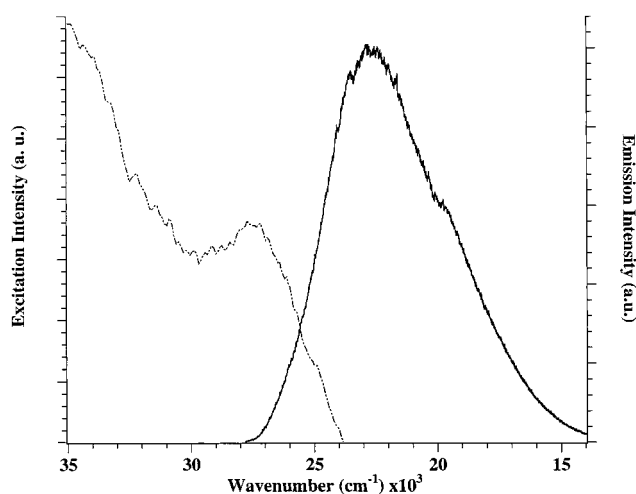

Figure 1. Solid-state excitation spectrum (dash−dotted line) taken at 77 K and emission spectrum (solid line) taken at 15 K of Me_2GaN_3.

Experimental Section

The title compound was synthesized according to literature methods and purified by sublimation.[13] Because the compound is air sensitive, all spectra were obtained from samples in sealed capillary tubes that were assembled in a drybox. All solution phase spectra were taken using distilled and degassed diethyl ether as the solvent.

Absorption Spectra. Absorption spectra at room temperature of the sample and reference in sealed quartz cuvettes were taken using a Shimazdu UV-260 spectrometer.

Emission Spectra. Luminescence spectra taken at 15 K were obtained using a Spex 1702 single monochromator equipped with an RCA C31034 photomultiplier tube. The signal was recorded with a Stanford Research System SR400 photon counter and stored on a computer. The 350.7 nm line from a Coherent I-300 krypton ion laser at 2 mW was used for excitation. Samples were cooled using an Air Products closed cycle helium refrigerator displex equipped with a thermocouple. The spectra were corrected for the instrument's response.

Excitation Spectra. Excitation spectra taken at 77 K were obtained with an ISA Spex model FL3−22 Fluorolog. The excitation spectrum was obtained while monitoring the emission at 22 000 cm^{-1}. The spectra are corrected for the xenon lamp intensity.

Emission Lifetime Measurements. Lifetime measurements were obtained by exciting the sample using the 355 nm line from a Quantel Brilliant Nd:YAG pulsed laser operating at 20 Hz. The emission decay was monitored at 22 000 cm^{-1} using the Spex single monochromator described above with the slits set at 150 μm.

Raman Spectra. Raman spectra were taken using the 514.5 nm line from a Coherent I-90 argon ion laser, at an excitation power of 150 mW. Spectra were obtained at room temperature using a Spex 1401 double monochromator equipped with an RCA C31034 photomultiplier tube. Data were collected with a Stanford Research System SR400 photon counter and stored on a computer.

Mass Spectra. Electron impact ionization mass spectra were obtained at the UCLA Mass Spectroscopy Facility.

Results and Discussion

I. Luminescence and Absorption Spectra. A. Solid-State Spectra. The emission spectrum of the solid Me_2GaN_3 polymer at 15 K shown in Figure 1 (solid line) consists of a broad unresolved band beginning at approximately 28 000 cm^{-1}, with a peak maximum at 22 300 cm^{-1}, and a full width at half-maximum of 6 700 cm^{-1}. A shoulder is observed at approximately 20 000 cm^{-1}. The excited-state lifetime at 15 K,
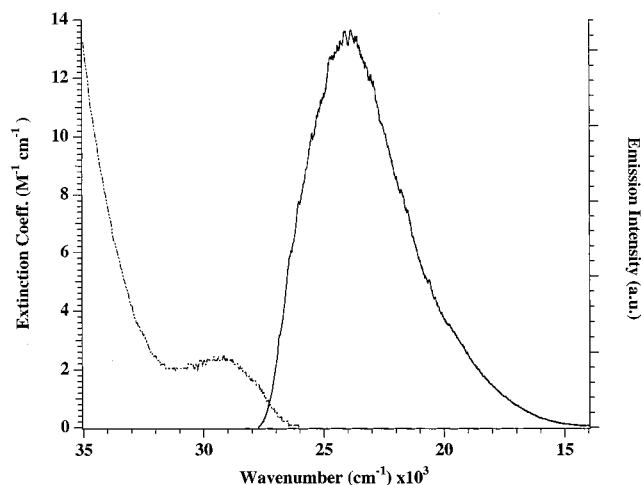
Figure 2. Solution absorption spectrum (dash−dotted line) taken at room temperature and frozen glass emission spectrum (solid line) taken at 15 K of Me_2GaN_3 in diethyl ether.

Table 1. Emission and Absorption Spectroscopic Data

|	solid phase	solution phase
Emission		
peak maximum (cm^{-1})	22300	24200
fwhm (cm^{-1})	6700	5200
lifetime (ns)	$\tau < 20$	$\tau < 20$
Absorption/Excitation		
peak maximum (cm^{-1})	27400	29150
extinct. coeff. ($M^{-1}\,cm^{-1}$)		2.4

monitored at 22 000 cm^{-1}, is less than the duration of the 20 ns laser pulse. Room-temperature luminescence is not observed from the solid-state sample.

The excitation spectrum of the polymeric solid at 77 K, shown in Figure 1 (dash-dotted line), consists of an unresolved broad band with a peak maximum at 27 400 cm^{-1}. The low energy side of the excitation spectrum and the high energy side of the emission spectrum overlap.

B. Frozen Glass. The emission spectrum of Me_2GaN_3 in a frozen glass of diethyl ether is similar to that obtained from the powder of the polymer but is blue shifted. The emission spectrum of Me_2GaN_3 in a frozen glass at 15 K, shown in Figure 2 (solid line), consists of an unresolved band beginning at 28 000 cm^{-1}, with a peak maximum at 24 200 cm^{-1}, and a full width at half-maximum of 5 200 cm^{-1}. The room-temperature electronic absorption spectrum (dash−dotted line), also included in Figure 2, shows a weakly allowed and unresolved band with a peak maximum at 29 150 cm^{-1} and a molar extinction coefficient of 2.4 $M^{-1}\,cm^{-1}$. The low energy side of the absorption spectrum and the high energy side of the emission spectrum overlap. No room-temperature emission was observed from the solution sample. The emission and absorption spectroscopic data in both the solid and solution phase have been collected in Table 1.

The similarity between the solid and solution phase spectra suggest that the same (or very similar) species are involved in both media. This result is somewhat surprising because the solid is a polymer with bridging azide ligands and the dissolved species could have been monomers. The results thus suggest that the species in solution are at least moderate chain length oligomers whose electronic structure is similar to that of the polymer. The small blue shift observed in the solution emission spectrum is consistent with oligomeric units whose chain length is long enough to give rise to polymer-like emission, but shifted to higher energy because of the shorter chain length. However,
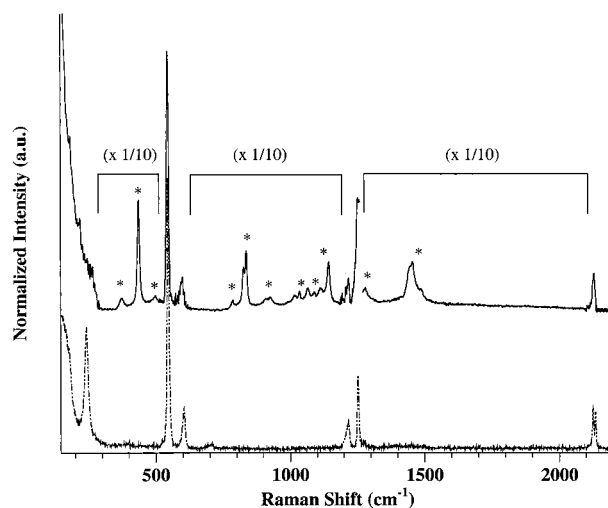
Figure 3. Solid-state (dash−dotted) and solution (solid line) Raman spectra of Me_2GaN_3. The solvent peaks have been reduced by a factor of 10 for clarity of presentation and are highlighted by an asterisk

in solution it would be expected that a range of chain lengths exists and that the emission occurs from a variety of oligomers. In this case, the emission bandwidth would be expected to be significantly larger than that from the polymer emission, contrary to that measured. The blue shift could also be caused by a solvatochromic shift. To investigate in more detail the nature of the dissolved species, vibrational spectra of Me_2GaN_3 as a solid and in solution were obtained.

II. Raman Spectra. The Raman spectrum (dashed line) of solid Me_2GaN_3 taken with 514.5 nm excitation is shown in Figure 3. The Raman intensities in the spectrum have been normalized to the most intense peak at 545 cm^{-1}, which was assigned as the symmetric GaC_2 stretching mode.[12,13]

A diethyl ether solution phase Raman spectrum (solid line) taken with 514.5 nm excitation is shown in Figure 3 for comparison with the spectrum of the solid polymer. The solution phase spectrum is also normalized to the 545 cm^{-1} vibrational peak. (The solvent peaks are reduced in intensity by a factor of 10, for clarity of presentation, and are highlighted by an asterisk.)

Comparison of the solid state versus solution Raman spectra reveals only very small differences in the vibrational frequencies. The 242 cm^{-1} $\delta(CGaC)$ vibrational mode from the solid sample appears as an unresolved broad shoulder in the solution spectrum. The 546 and 604 cm^{-1} $\nu_s(CGaC)$ normal modes show no significant loss of resolution and only small decreases in frequency, to 542 and 598 cm^{-1}, respectively. The vibrational modes at 1215 cm^{-1} $\delta(CH_3)$ and 1251 cm^{-1} $\nu_s(N_3)$ do not show any change in frequency. In addition, the normal modes assigned as the asymmetric azide $\nu_{as}(N_3)$ stretching vibrations at 2125 and 2135 cm^{-1} show no frequency shift between solid and solution. The main effect that the solvent imparts to these vibrations is a loss of resolution between the individual peaks.

The Raman vibrational spectra show that the normal modes in the solid polymer remain essentially the same in solution. If the polymer dissociated into monomeric units in solution, the geometry and electronic structure would be very different and the vibrational frequencies would change accordingly, contrary to the experimental results. The very small frequency shifts (≤ 6 cm^{-1}) that are observed are probably caused by solvation. The absence of major shifts upon dissolution suggests that the species in solution are not monomeric, but are similar to those in the solid. The presence of oligomeric moieties provides a reasonable

explanation for the small energy shift in the electronic spectra and the small frequency shifts in the Raman spectra.

III. Mass Spectroscopy. To investigate the structure of the oligomeric species, a sample of the solid was used for mass spectroscopic analysis. The electron impact ionization mass spectrum of the solid shows extensive fragmentation, with observed mass peaks ranging from 99 to 533 amu. The most intense peak is observed at 433 amu, and the highest mass value is 533 amu.

The most abundant mass (433 amu) corresponds to a $[Me_2GaN_3]_3$ trimeric subunit. Previous workers observed a mass fragment at 412 amu corresponding to $[Me_2GaN_3]_3$ less one methyl group, but no higher mass fragments were reported.[1,12] The highest mass peak at 533 amu can be assigned as $[Me_2GaN_3]_4$ less (N_3). No mass fragments were observed at 142 amu corresponding to monomeric Me_2GaN_3.

It is possible that $[Me_2GaN_3]_3$ trimers are present in both the polycrystalline solid and in solution and thus may contribute to the luminescence in both the liquid and solid states. However, the crystal structure shows that the structure is a coiled polymer in the solid. It is not possible to determine with certainty the structure of the emitting species. The similarities of the Raman spectra and of the emission spectra in solution and as a solid shows that similar species (such as moderate length oligomers in solution and polymer in the solid) are the luminophores in both cases.

IV. Assignment of the Luminescence. The lowest energy electronic excited states of metal−azide compounds have not been well studied.[14−20] Based on the limited data, the usual assignment involves azide ligand to metal charge-transfer character. In the case of $W(CO)_5N_3{}^-$, the lowest energy state was assigned as LMCT with some admixture of d−d transi-

tions.[16] In the case of the main group metal hexacoordinate homoleptic azide complexes $[Sn(N_3)_6]^{2-}$ and $[Pb(N_3)_6]^{2-}$, the lowest energy excited electronic states were assigned to LMCT transitions, but other electronic transitions were also suspected to be present.[20] The authors concluded that in addition to the LMCT transition, the presence of intra-ligand and ligand-to-ligand charge transfer could not be discounted.

To obtain insight into the low energy electronic transitions in gallium−azide complexes, semiempircal PM3 molecular orbital calculations were carried out using SPARTAN.[21] The emitting species is a polymer or oligomer. As a model, the calculations were carried out on a trimeric $[Me_2GaN_3]_3$ unit. The bond lengths from the crystal structure of the polymer were used.[1] The calculations show that there is a cluster of occupied orbitals within a few tenths of an electronvolt of the HOMO that includes an orbital that is mainly azide π nonbonding in character. This cluster of occupied orbitals also contains a gallium-centered orbital. The lowest unoccupied molecular orbital is mainly gallium 4p orbital in character, with a much smaller but significant contribution from the azide π^* antibonding orbitals. The lowest unoccupied molecular orbital, in addition, contains a smaller amount of the gallium 4s orbital. These results suggest that the lowest energy electronic transition has a large component of $(N(\pi_{nb}) \rightarrow Ga_{4p})$, ligand-to-metal charge-transfer character, and, to a lesser extent, gallium centered $(d \rightarrow p)$ and ligand-to-ligand charge-transfer character. The short $(\tau < 20$ ns) luminescence lifetime suggests that the transition is spin allowed.

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