Luminescence Phenomena and Solid-State Structures of Trimethyl- and Triethylgallium**

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Dedicated to Professor Dr. Rainer Mattes on the occasion of his 65th birthday

Trialkylgallium compounds are widely used as precursors in chemical vapor deposition (CVD) processes for the generation of thin layers of gallium semiconductor compounds such as GaAs or GaN.[1] Although triethylgallium ($GaEt_3$) was first described in 1932,[2] to date there have been no reports about its remarkable luminescent behavior and decomposition upon cooling to liquid-nitrogen temperature, which we present herein. We also investigate these phenomena in the context of the solid-state structures of this class of compounds.

We observed intriguing luminescence phenomena and decomposition of $GaEt_3$, when we attempted to degas a 100-mL sample (electronic grade purity) to transfer part of it under vacuum for a crystal-growth experiment in the course of structure determination. A large number of little flashes were observed during the freezing process in liquid nitrogen, but even more intense flashes occurred after removing the coolant (Figure 1b). The light emissions start about one minute after the sample is removed from the coolant, that is, when the temperature is between -180 and $-150\,^\circ C$, and stop when the sample reaches an average temperature of about $-100\,^\circ C$. The light emission is accompanied by a sound resembling the cracking of ice, which indicates the origin of the effect; triboluminescence[3] caused by breaking of the $GaEt_3$ crystals.

Triboluminescence occurs in certain crystalline phases when mechanical stress is applied (in our case because of thermal contraction or expansion of the polycrystalline sample). The light emission in these cases is said to be caused by the charge separation over the new surfaces generated by breaking a crystal, the discharge of such accumulated charge, and the subsequent excitation of the gas between the new surfaces. This explanation is consistent with our observation that $GaEt_3$ samples handled under inert gases (He, Ne, Ar, Xe) show luminescence, and that the observed emission spectrum (Figure 2) contains the atomic emission spectrum of the corresponding noble gas. Only for xenon were other lines observed, but these could not be identified to date. This observation is fully consistent with other reports on the dependence of triboluminescence spectra on the present gas atmosphere.[3]

Figure 1. a) Two samples of $GaEt_3$. Left: a pure sample; Right: a sample after 15 freeze–thaw cycles under argon, b) the triboluminescence flashes which occur upon warming a sample of $GaEt_3$ under argon that had been frozen in liquid nitrogen.

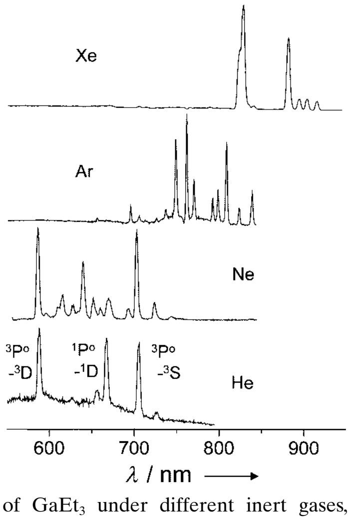

Figure 2. Luminescence spectra of $GaEt_3$ under different inert gases, recorded about 1 min after removing a 100-mL sample from cooling ($-196\,^\circ C$). For the lower spectrum (He), an assignment of some lines is given.

The decomposition of the sample with emission is easily seen by a blackening of the liquid, which becomes darker after each freeze–thaw cycle (Figure 1a). In a neon atmosphere, the strongest decomposition is observed. Finally a fine, black

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precipitate of elemental Ga settles after standing for a few days. Thus, this physical effect of luminescence is accompanied by a chemical change of the sample. To understand this decomposition in more detail, we repeated the freeze–thaw cycles about 100 times with a small sample of neat $GaEt_3$ in an NMR spectroscopy tube and measured the ^1H and ^{13}C NMR spectra before and after this treatment. Small amounts of ethane and even smaller amounts of ethene could be detected. The gases could be accumulated and isolated by repeating the experiment about 30 times with a 100-mL sample and pumping the volatile components through a series of cold traps on a high vacuum line. Tiny amounts of ethane and ethene passed through a −78 °C trap and were identified by gas-phase IR spectroscopy and NMR spectroscopy. Apart from the black precipitate (which is finely divided gallium), no other decomposition product was found, in particular no dihydrogen gas or butane (from dimerized ethyl substituents of the $GaEt_3$). Decomposition of the homologous $AlEt_3$ by photochemical processes is known to yield elemental aluminum and ethane[4] and therefore we anticipated a similar process in our case. This process parallels the photochemical initialization of chemical reactions by triboluminescence, such as detonations, which were previously reported.[5]

We could verify this hypothesis by directly exposing $GaEt_3$ in a glass tube to a neon discharge, to simulate the conditions of discharge and light emission involved in triboluminescence. In these experiments samples of liquid $GaEt_3$ at −78 °C and solid $GaEt_3$ at −110 °C were placed in a neon atmosphere (about 5 mbar), which was excited about 5 cm above the $GaEt_3$ surface by applying a weak, high frequency field, so that the typical red neon light was observable. Under these conditions the same decomposition products (ethane, traces of ethene, and a small amount of a black gallium precipitate) were observed.

To date we could not find other gallium alkyls showing triboluminescence under these conditions, but we have tested only tri-*n*-butylgallium, tri-*tert*-butylgallium, and trimethylgallium. The reason for this different behavior can be rationalized by the solid-state structures, as $GaEt_3$ is the only compound crystallizing in an acentric and polar space group, which was often described as a prerequisite for triboluminescence[6] and the crystals of most triboluminescent compounds are found to adopt acentric space groups (exceptions are known, but are disputed).[3] By contrast to $GaEt_3$, $GaMe_3$ crystallizes centrosymmetrically and both butylgallium compounds are glassy solids.

Mechanical energy is the source of energy for the observed triboluminescence in $GaEt_3$, but without application of external mechanical stress. For an improved understanding of the cracking of the galliumtrialkyl compounds during freezing and thawing, we looked at the thermal contraction of these compounds. $GaEt_3$ and $GaMe_3$ undergo an enormous shrinkage during the liquid–solid phase transition. According to our crystallographic data (see below) the density in the solids at −130 °C is 24.5 % and 26.2 % higher than that of liquid $GaEt_3$ ($\rho(30\,°C) = 1.058\ g\,cm^{-3}$) and $GaMe_3$ ($\rho(25\,°C) = 1.151\ g\,cm^{-3}$), respectively.[7] For $GaEt_3$ we observed an almost linear increase in density of 12 % while cooling the liquid from +30 to −82 °C, a spontaneous rise in density of 10 % during the liquid–solid phase transition at −82 °C, but only a small thermal contraction of 2 % in the solid state of $GaEt_3$ by further cooling to −145 °C. These density changes were determined by crystallographic measurement of the cell dimensions at five temperatures between −85 °C (i.e. near the melting point of −82 °C, $\rho = 1.307\ g\,cm^{-3}$) and −145 °C ($\rho = 1.331\ g\,cm^{-3}$). This large shrinkage during solidification probably builds up the strain that is later released by cracking of the crystals, which leads to the observed triboluminescence. The reason for the relatively high density of the solids of $GaEt_3$ and $GaMe_3$ becomes obvious from their crystal structures, which will now be described.

The solid-state structure of $GaEt_3$ (Figure 3) is quite complicated,[8] as it comprises layers of wavelike networks of the four independent molecules in the unit cell. The Ga atoms are between 2.50 and 3.16 Å away from the H atoms of their next neighbors. The corresponding Ga···C distances, which describe the relevant contacts, lie between 3.087–3.593 Å. Each of the Ga atoms is weakly coordinated by two such intermolecular Ga···C contacts, apart from Ga1, which is involved in only one such short interaction. Note that the Ga atoms form contacts to both sorts of C atoms, methylene and methyl carbon atoms, of the neighboring molecules. All $GaEt_3$ molecules are present in conformations with almost planar GaC_6 skeletons and no gauche conformation for CCGaC units occurs. Three of the four molecules are found in a propeller-like arrangement and only the $GaEt_3$ molecule containing Ga3 does not adopt approximate C_3 symmetry and has two ethyl groups pointing towards each other. The wide Ga-C-C angles (between 113.3(2) and 118.8(2)°) resemble the B-C-C angles in the structure of solid

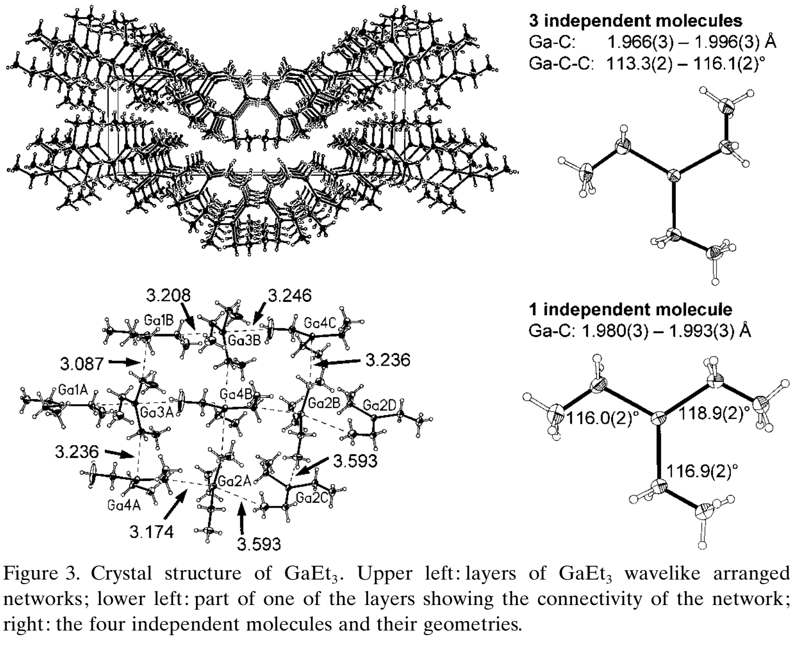

Figure 3. Crystal structure of $GaEt_3$. Upper left: layers of $GaEt_3$ wavelike arranged networks; lower left: part of one of the layers showing the connectivity of the network; right: the four independent molecules and their geometries.

BEt_3 (118.7–119.3°), which was explained by hyperconjugation of the boron p orbital into C-H orbitals.[9]

With the structure determination and ab initio calculations of a $GaMe_3$ dimer, we wanted to provide more detailed knowledge about the intermolecular forces responsible for the thermal contraction of the gallium alkyls in general and thus the triboluminescence of $GaEt_3$. The crystal structure of $GaMe_3$ was unknown to date, as well as the structure of BMe_3, while the structures of the other trimethyl compounds of the group 13 elements are described. By chance, the determination of the structure of $GaMe_3$ was simultaneously and independently undertaken by two other groups but, interestingly, two different structures of $GaMe_3$ were obtained; a monoclinic one ($\rho(-143\,^{\circ}C) = 1.444\ g\,cm^{-3}$, space group $C2/c$, two independent molecules) in the hands of Boese, Parsons, and co-workers[10] and a tetragonal one from our experiments ($\rho(-140\,^{\circ}C) = 1.453\ g\,cm^{-3}$, space group $P4_2/n$, Figure 4).[8] Boese and co-workers also determined the structure of BMe_3.[10] With these newly established data, the structures of the trimethyl compounds of the group 13 elements are found to differ markedly from one another: BMe_3 is monomeric,[10] $AlMe_3$ crystallizes as a dimer with two bridging methyl units, with short Al–C distances and four-coordinate Al atoms,[11, 12], whereas $InMe_3$[13] and $TlMe_3$[14] are arranged into tetramers with considerably longer metal–carbon distances, with the metal atoms adopting a primary trigonal-planar coordination, while the weaker intermolecular interactions are in perpendicular direction to the primary coordination plane.

Our tetragonal structure of $GaMe_3$ is closely related to the structures of $InMe_3$ and $TlMe_3$, which are also tetragonal and tetrameric. The gallium atoms in $GaMe_3$ are planar (sum of angles about Ga 359.9°) and weakly coordinated to a methyl group of a neighboring molecule, with Ga⋯H distances between 2.95–2.96 Å and a Ga⋯C distance of 3.134 Å. Surprisingly this distance is longer than that of $InMe_3$ (In⋯C 3.083(12) Å)[13] and shorter than in $TlMe_3$ (Tl⋯C 3.16 Å).[14] The interactions between the metal atoms and the methyl groups of molecules of other tetramers are much longer than those within the tetramers (In⋯C 3.558(15) and Tl⋯C 3.31 Å) and are even longer in $GaMe_3$ (3.647(3) Å). These weak contacts arrange the $GaMe_3$ tetramers into endless 2D networks.

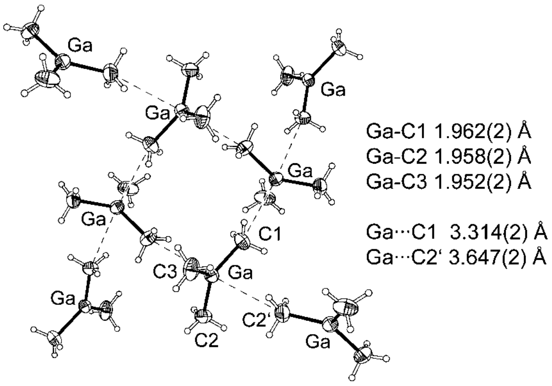

Figure 4. A tetramer of $GaMe_3$ and its connectivity in the layers of tetragonal crystals.

Although less symmetrical, the monoclinic structure of $GaMe_3$[10] can also be described as containing tetrameric units (Ga⋯C 3.069 and 3.210 Å), which are also part of a large 2D network formed by longer Ga⋯C contacts of 3.234 and 3.523 Å, but these rather similar distances make a clear distinction between the longer and shorter distances impossible. In our tetragonal structure of $GaMe_3$ the order of Ga–C bond lengths is fully consistent with the involvement of the respective methyl groups in secondary bonding. They are: Ga-C3 1.952(3) Å (no Ga⋯C contact), Ga-C2 1.958(2) Å (weak Ga⋯C2′ contact of 3.647(2) Å) and Ga-C1 1.962(2) Å (short Ga⋯C(1)′ contact of 3.314(2) Å). They are only marginally shorter than in gaseous $GaMe_3$ (1.967(2) Å),[12], which shows that the intermolecular interactions do not strongly distort the structure of the monomers.

As no detailed investigations on the cause of these interactions have been reported to date, we performed quantum chemical calculations. For computational feasibility we chose to model the interactions in the tetrameric structure by only considering a dimer of $GaMe_3$, that is, to model only one of the interactions between a Ga center and the methyl group of another $GaMe_3$ molecule. The structure of the $GaMe_3$ dimer was optimized and the interaction energy analyzed at the local MP2/TZVP level.[15] The optimized structure is shown in Figure 5 and, apart from a slight twist, the geometry appears to be very similar to a fragment of the tetrameric unit in the crystal. The calculated intermolecular Ga⋯C distance is in the dimer 3.206 Å and 3.134(1) Å in the tetramer of solid, tetragonal $GaMe_3$. The calculations reproduce the slight elongation of the Ga–C bond of the coordinated methyl group involved in the dimer/tetramer formation, as well as the staggered arrangement of the hydrogen atoms in this methyl group, relative to the GaC_3 skeleton of the neighboring $GaMe_3$ molecule. The calculated interaction energy between the $GaMe_3$ molecules is 11.4 kJ mol^{-1}.

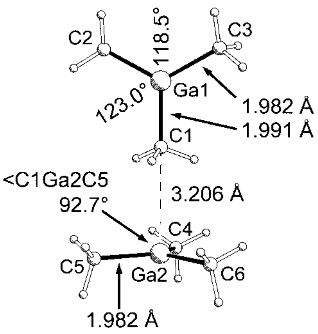

Figure 5. Calculated geometry of the dimer of $GaMe_3$ (LMP2/TZVP).

The interaction energy obtained at the LMP2 level can be partitioned into the following components: The SCF contribution, which should contain the major part of any covalent, ionic, or electrostatic contributions. This contribution is calculated to be 3.4 kJ mol^{-1}. The remaining part is the correlation contribution of the interaction energy and it can be separated into different classes, according to reference [15a]. The calculated attractive contributions for dispersion are 7.5 kJ$\,$mol^{-1}, for ionic excitations 4.2 kJ$\,$mol^{-1}, and for exchange dispersion 0.0 kJ$\,$mol^{-1}. In addition, there is a repulsive contribution of -3.8 kJ$\,$mol^{-1}, which corresponds to the reduced intramonomer correlation when the monomers approach each other. As the SCF interaction can be reproduced by a model, which only takes into account the classical electrostatic interactions between the $GaMe_3$ monomers without any induction or dispersion effects,[16] we conclude that the interaction has no covalent character, but consists of dispersion and ionic correlation contributions, as well as classical electrostatic contributions.

The topology of the electron density in the region of this $Ga\cdots C$ interaction shows a bond-critical point on the line connecting the Ga atom and the C atom of the neighboring methyl group. This point indicates that there is no interaction of the agostic type which would require $Ga\cdots H$ interactions with bond-critical points between Ga and H atoms.[17] Furthermore, the calculated Ga-C-H angles at the interacting methyl group are only slightly wider than the other Ga-C-H angles in the dimer.

We showed a connection between weak intermolecular forces leading to a large temperature dependence of the density and thus to mechanical properties, which causes the triboluminescence of $GaEt_3$, as this crystallizes in an polar, acentric space group and which is distinct from the non-triboluminescent $GaMe_3$. Many details remain still unclear and deserve further investigation. These include the chemistry involved in the decomposition of $GaEt_3$ and the interaction of $GaEt_3$ with xenon.

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[8] Crystal data for $GaMe_3$ and $GaEt_3$: Single cylindrical crystals of $GaMe_3$ and $GaEt_3$ of 0.3-mm diameter were grown in the cryostream of a Nonius DIP 2020 diffractometer by slowly cooling the melt sealed in a thin-walled glass capillary after establishing a solid–liquid equilibrium and optically selecting a single suitable seed crystal by repeated crystallization–melting cycles. Intensity corrections were applied using the program SCALEPACK.[18] The structures were solved by direct methods and refined by least-squares methods on F^2.[19] C and Ga atoms were refined with anisotropic thermal displacement factors, H atoms isotropically (all CH_3 groups in $GaMe_3$ were restrained to have local C_3 symmetry, in $GaEt_3$ only one CH_3 group had to be restrained to local tetrahedral symmetry). $GaMe_3$: GaC_3H_9, tetragonal, $P4_2/n$, $a = 12.9532(3)$, $c = 6.2588(1)$ Å, $\beta = 90.8522(5)°$, $V = 1050.13(4)$ Å^3, $Z = 8$, $\rho_{calc} = 1.453$ g$\,$cm^{-3}, $\lambda = 0.71073$ Å, $2\theta_{max} = 63°$, $T = 133(2)$ K, $\mu = 5.059$ mm^{-1}. 28820 measured and 1684 independent reflections ($R_{int} = 0.041$). $F(000) = 464$, 110 parameters, $R_1 = 0.0336$ for 1526 reflections with $F_o > 4\sigma(F_o)$ and $wR_2 = 0.0882$ for all 1684 data. Max./min. residual peaks -0.62/0.70 e$\,$Å^{-3}. $GaEt_3$: GaC_6H_{15}, monoclinic, Pc, $a = 8.4514(1)$, $b = 25.1534(3)$, $c = 7.4473(1)$ Å, $V = 1582.98(3)$ Å^3, $Z = 8$, $\rho_{calc} = 1.317$ g$\,$cm^{-3}, $\lambda = 0.71073$ Å, $2\theta_{max} = 55°$, $T = 133(2)$ K, $\mu = 3.375$ mm^{-1}. 62175 measured and 6946 independent reflections ($R_{int} = 0.0218$). $F(000) = 656$, 485 parameters, $R_1 = 0.0249$ for 6806 reflections with $F_o > 4\sigma(F_o)$ and $wR_2 = 0.0602$ for all 6946 data. Max./min. residual peaks -0.36/0.28 e$\,$Å^{-3}. The structure of $GaEt_3$ was refined as a racemic twin with the major component contributing 53.3(10)%. CCDC-163477 ($GaMe_3$) and CCDC-163478 ($GaEt_3$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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