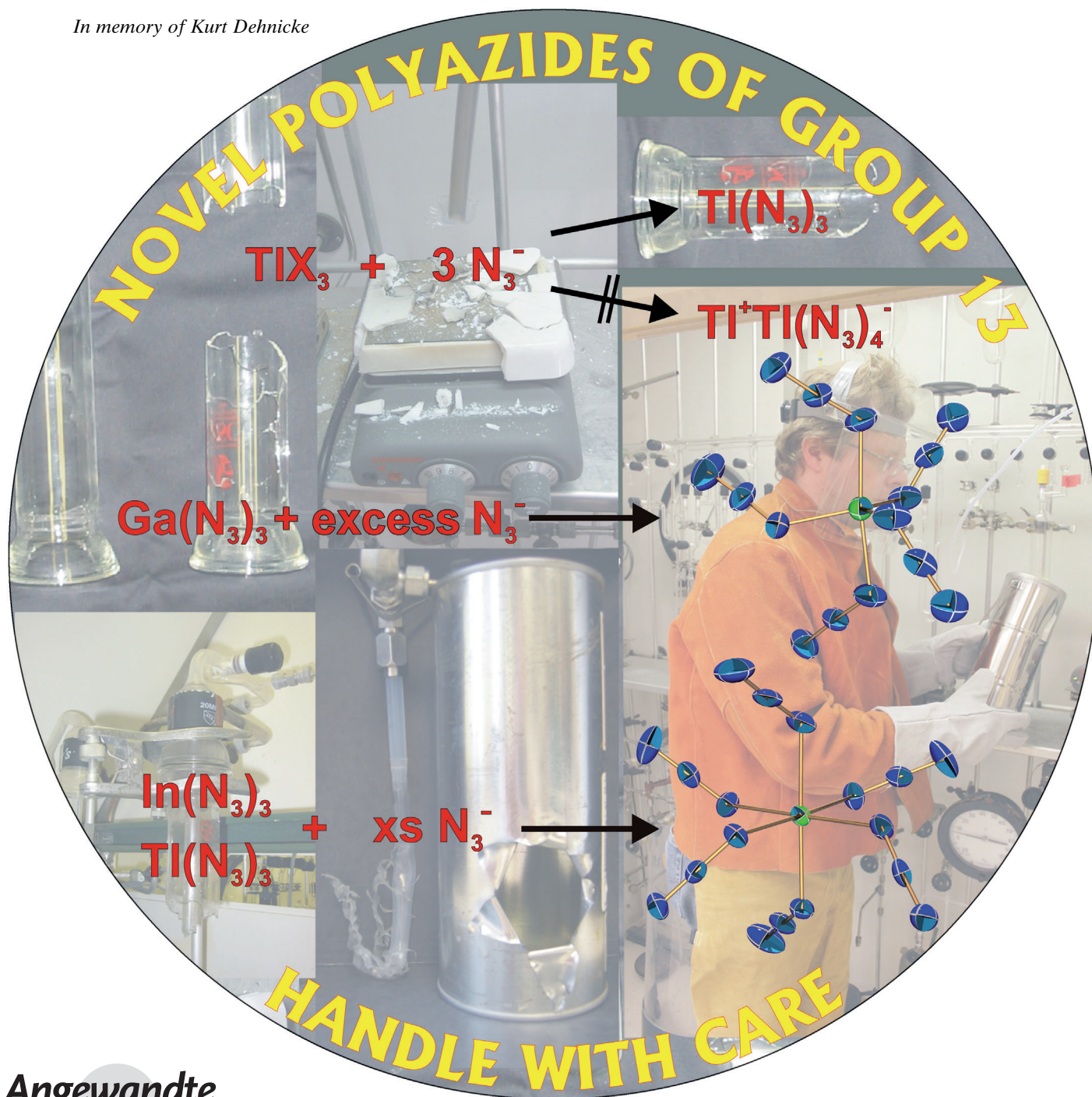


Preparation and Characterization of the Binary Group 13 Azides $M(N_3)_3$ and $M(N_3)_3 \cdot CH_3CN$ ($M = Ga, In, Tl$), $[Ga(N_3)_5]^{2-}$, and $[M(N_3)_6]^{3-}$ ($M = In, Tl$)**

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In memory of Kurt Dehnicke

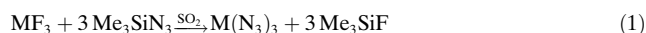


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There has been much interest in polyazido compounds during the last two decades.^[1–18] In particular, the potential of Group 13 azides as precursors for the synthesis of the corresponding nitrides has been studied in great detail owing to their usefulness for semiconductor and optoelectronic applications. Although most of these efforts were devoted to gallium azides,^[19,20] aluminum and indium azides were also explored.^[19,21] For thallium, the monoazide is well-known and is an impact- and highly friction-sensitive compound, similar in properties to silver azide and lead diazide.^[22] However, little is known about the triazide. To our knowledge, the only previous report deals with the formation of a highly explosive yellow solid, formed by the reaction of $\text{Ti}(\text{OH})_3$ with HN_3 .^[23] Based on its elemental analysis, it had the composition $\text{Ti}(\text{N}_3)_2$ and was proposed to be the mixed $\text{Ti}^{\text{I}}/\text{Ti}^{\text{III}}$ salt $\text{Ti}[\text{Ti}(\text{N}_3)_4]$, but this interpretation was subsequently questioned.^[22]

The syntheses and characterization of molecules with a high number of azido groups is very challenging owing to the high energy content of the azido group, which is responsible for their frequently encountered explosive and shock-sensitive nature. Herein, we communicate the syntheses of $\text{Ga}(\text{N}_3)_3$, $\text{In}(\text{N}_3)_3$, and $\text{Tl}(\text{N}_3)_3$ in SO_2 and CH_3CN solutions, their 1:1 adducts with CH_3CN , and the first examples of multiply charged Group 13 polyazido anions, $[\text{Ga}(\text{N}_3)_5]^{2-}$, $[\text{In}(\text{N}_3)_6]^{3-}$, and $[\text{Tl}(\text{N}_3)_6]^{3-}$. We also report the crystal structures of the tetraphenylphosphonium salts of the $[\text{Ga}(\text{N}_3)_5]^{2-}$, $[\text{In}(\text{N}_3)_6]^{3-}$, and $[\text{Tl}(\text{N}_3)_6]^{3-}$ anions and the vibrational spectra and electronic structure calculations for all the compounds.

In analogy to our reported syntheses of inorganic polyazides,^[14] the trifluorides GaF_3 , InF_3 , and TlF_3 were treated with an excess of trimethylsilyl azide in SO_2 . This procedure resulted in rapid and complete fluoride–azide exchange [Eq. (1), $\text{M} = \text{Ga}, \text{In}, \text{Tl}$].



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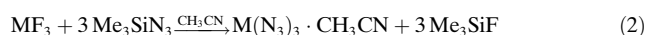
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[**] This work was funded by the Air Force Office of Scientific Research, the Office of Naval Research, the Defense Threat Reduction Agency, and the National Science Foundation. We thank Profs. G. Olah and S. Prakash for their steady support, and Drs. W. Wilson and R. Wagner for their help and stimulating discussions. Grants of computer time from the Department of Defense High Performance Computing Modernization Program at the Engineer Research and Development (ERDC) and Navy Department of Defense Supercomputing Centers are gratefully acknowledged.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201103101>.

Removal of the volatile compounds (SO_2 , Me_3SiF , and excess Me_3SiN_3) under reduced pressure at -20°C produces the neat triazides as colorless to orange solids. The azides $\text{Ga}(\text{N}_3)_3$, $\text{In}(\text{N}_3)_3$, and $\text{Tl}(\text{N}_3)_3$ are stable at room temperature but are very shock-sensitive. While $\text{Ga}(\text{N}_3)_3$ is the least sensitive of the three compounds, it is still dangerous, and we encountered several explosions while handling small samples. $\text{In}(\text{N}_3)_3$ and especially $\text{Tl}(\text{N}_3)_3$ are more treacherous and tend to explode violently upon the slightest provocation (agitation, rapid change in temperature and/or pressure). The physical properties of $\text{Ga}(\text{N}_3)_3$ and $\text{In}(\text{N}_3)_3$ are in excellent agreement with previous literature reports.^[19]

When CH_3CN instead of SO_2 was used as solvent for the reactions of GaF_3 , InF_3 , and TlF_3 with excess Me_3SiN_3 , colorless to orange solutions were obtained. Removal of all volatile materials (Me_3SiF , CH_3CN , and excess Me_3SiN_3) resulted in the isolation of the acetonitrile adducts of the triazides as pale yellow to orange solids [Eq. (2), $\text{M} = \text{Ga}, \text{In}, \text{Tl}$].



It was not possible to remove the acetonitrile in a vacuum of 10^{-4} Torr at ambient temperature. Even after exposure to vacuum for 24 h, samples of $\text{M}(\text{N}_3)_3 \cdot \text{CH}_3\text{CN}$ showed virtually no mass loss.

The neat acetonitrile adducts of the triazides $\text{M}(\text{N}_3)_3 \cdot \text{CH}_3\text{CN}$ are less dangerous than the donor-free triazides but are still shock-sensitive and can explode violently upon provocation (e.g., agitation). The stabilization of these triazides by adduct formation with CH_3CN is in accord with previous reports that $\text{Ga}(\text{N}_3)_3$ is a strong Lewis acid and can form stable, structurally characterized adducts with either one molecule of trialkyl amine^[19] or three molecules of pyridine,^[19,20] yielding pseudo-tetrahedral or pseudo-octahedral *mer*-configuration adducts, respectively.

All attempts to grow single crystals of the triazides or their acetonitrile adducts by recrystallization were unsuccessful. The identity of the compounds $\text{M}(\text{N}_3)_3$ and $\text{M}(\text{N}_3)_3 \cdot \text{CH}_3\text{CN}$ was established by the observed material balances, vibrational spectra, and by their conversions with tetraphenylphosphonium azide into salts of the previously unknown anions $[\text{Ga}(\text{N}_3)_5]^{2-}$, $[\text{In}(\text{N}_3)_6]^{3-}$, and $[\text{Tl}(\text{N}_3)_6]^{3-}$ which were characterized by their crystal structures.

The recording of the vibrational spectrum of the neat triazides was very challenging owing to their extreme shock-sensitivity. In spite of these difficulties, we succeeded in recording Raman spectra of microcrystalline samples of all three neat triazides as well as an IR spectrum of $\text{Ga}(\text{N}_3)_3$.

The vibrational frequencies and intensities observed for microcrystalline $\text{M}(\text{N}_3)_3$ and $\text{M}(\text{N}_3)_3 \cdot \text{CH}_3\text{CN}$ ($\text{M} = \text{Ga}, \text{In}, \text{Tl}$) are compared with those calculated for the free molecular species at the MP2/SBKJ + (d) and B3LYP/SBKJ + (d) levels of theory in Tables S6–S7 of the Supporting Information.

The MP2 and B3LYP calculations result in minimum-energy structures of C_{3h} symmetry for all three neat planar triazides $\text{M}(\text{N}_3)_3$. However, another isomer of C_s symmetry and only slightly higher energy is also found for the three compounds. At the B3LYP/SBKJ + (d) level, the C_s isomer of

$\text{Ga}(\text{N}_3)_3$ is only $1.3 \text{ kcal mol}^{-1}$ (MP2: $2.5 \text{ kcal mol}^{-1}$) higher in energy, the one of $\text{In}(\text{N}_3)_3$ is only $0.7 \text{ kcal mol}^{-1}$ (MP2: $1.1 \text{ kcal mol}^{-1}$) higher in energy, and the one of $\text{Tl}(\text{N}_3)_3$ was found to be only $0.7 \text{ kcal mol}^{-1}$ (MP2: $0.6 \text{ kcal mol}^{-1}$) higher in energy. The two structures are very similar (see Table S1 Supplementary Material) and deviate from each other only in the orientation of one azido group. The small energy differences of less than 3 kcal mol^{-1} between the C_{3h} and C_s structures demonstrate the structural flexibility of the azido ligands. The agreement between the predicted and observed vibrational spectra is only fair and indicates that the neat triazides are strongly associated in the solid state, in accord with their low solubilities and volatilities.

For $\text{Ga}(\text{N}_3)_3 \cdot \text{CH}_3\text{CN}$ and $\text{In}(\text{N}_3)_3 \cdot \text{CH}_3\text{CN}$ (Figure 1), the MP2/SBKJ + (d) and B3LYP/SBKJ + (d) calculations result in minimum-energy structures of C_3 symmetry, resembling the crystal structure known for the $\text{Ga}(\text{N}_3)_3 \cdot \text{NR}_3$ adducts.^[19] The predicted minimum-energy structure of $\text{Tl}(\text{N}_3)_3 \cdot \text{CH}_3\text{CN}$ is of C_s symmetry at the B3LYP/SBKJ + (d) level and of C_1 symmetry at the MP2/SBKJ + (d) level of theory (see the Supporting Information).

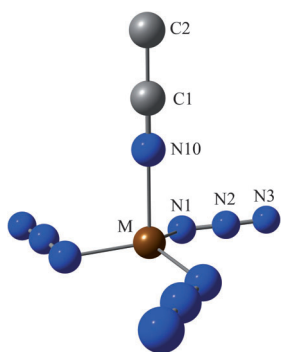


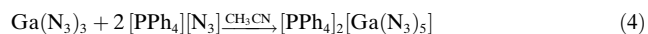
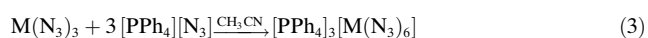
Figure 1. Calculated C_3 structure of the acetonitrile adducts $\text{M}(\text{N}_3)_3 \cdot \text{CH}_3\text{CN}$ ($\text{M} = \text{Ga}, \text{In}$). Bond lengths and angles are listed in the Supporting Information.

As found for other binary polyazides,^[8–15,19–21] the neutral polyazides can be stabilized either by the formation of donor–acceptor adducts with Lewis bases or by anion formation, which increases the ionicity of the azido groups. Because an ionic azide group possesses two double bonds while a covalent azido group has a single and a triple bond, increasing the ionicity of the existing azido ligands by further azide addition makes the breaking of an N–N bond more difficult and enhances the activation energy barrier toward catastrophic N_2 elimination. The Group 13 $\text{M}(\text{N}_3)_3$ molecules are all strong Lewis acids and, in principle, could add one, two, or three azide ions to form the $[\text{M}(\text{N}_3)_4]^-$, $[\text{M}(\text{N}_3)_5]^{2-}$, and $[\text{M}(\text{N}_3)_6]^{3-}$ anions, respectively. In the case of boron, the maximum coordination number (CN) is four and, therefore, only the $[\text{B}(\text{N}_3)_4]^-$ anion is formed.^[1a,24] In contrast, Al, Ga, In, and Tl prefer CNs larger than four, preferably six, and cases of $\text{CN} = 4$ are only known for $[\text{Al}(\text{N}_3)_4]^{2-}$ and $[\text{Ga}(\text{N}_3)_4]^-$.^[19] Since the azido ligand, unlike the nitrate ligand,^[25] is only monodentate, in $[\text{M}(\text{N}_3)_4]^-$ an increase of $\text{CN} = 4$ to $\text{CN} = 6$ requires the addition of two extra donor molecules. Two

well-characterized examples for the latter case are $[\text{Al}(\text{N}_3)_4(\text{thf})_2]^-$ and $[\text{In}(\text{N}_3)_4(\text{pyr})_2]^-$ ($\text{pyr} = \text{pyridine}$).^[19]

To examine the stabilization of the very explosive triazides $\text{M}(\text{N}_3)_3$ ($\text{M} = \text{Ga}, \text{In}, \text{Tl}$) by azide addition, these compounds were treated with one equivalent of tetraphenylphosphonium azide in acetonitrile. Under these conditions, no evidence for the formation of tetraazido anions $[\text{M}(\text{N}_3)_4]^-$ was found. Instead, a 1:1 mixture of $[\text{PPh}_4][\text{Ga}(\text{N}_3)_5]$ and the unreacted triazide was obtained for $\text{Ga}(\text{N}_3)_3$. In the case of $\text{In}(\text{N}_3)_3$ and $\text{Tl}(\text{N}_3)_3$, 1:2 mixtures of the corresponding hexaazido compounds $[\text{PPh}_4][\text{M}(\text{N}_3)_6]$ and the triazides were obtained.

The triazides were then treated with three equivalents of $[\text{PPh}_4][\text{N}_3]$ in acetonitrile. While for $\text{In}(\text{N}_3)_3$ and $\text{Tl}(\text{N}_3)_3$ the pure hexaazido salts $[\text{PPh}_4][\text{M}(\text{N}_3)_6]$ were formed [Eq. (3) ($\text{M} = \text{In}, \text{Tl}$)], in the case of $\text{Ga}(\text{N}_3)_3$ only 1:1 mixtures of the pentaazide $[\text{PPh}_4][\text{Ga}(\text{N}_3)_5]$ and unreacted $[\text{PPh}_4][\text{N}_3]$ were obtained [Eq. (4)].



$[\text{PPh}_4][\text{In}(\text{N}_3)_6]$ and $[\text{PPh}_4][\text{Tl}(\text{N}_3)_6]$ were isolated as room-temperature-stable, crystalline solids of yellow and orange color, respectively. $[\text{PPh}_4][\text{Ga}(\text{N}_3)_5]$ was isolated as colorless crystals that are stable at room temperature. Because of the increased ionicity of their azido ligands and the presence of two or even three large counterions per anion, which diminishes shock propagation, all three compounds are much less sensitive and explosive than their parent compounds $\text{M}(\text{N}_3)_3$ ($\text{M} = \text{Ga}, \text{In}, \text{Tl}$) and could be manipulated in our study at room temperature without explosion. The $[\text{PPh}_4][\text{Ga}(\text{N}_3)_5]$, $[\text{PPh}_4][\text{In}(\text{N}_3)_6]$, and $[\text{PPh}_4][\text{Tl}(\text{N}_3)_6]$ salts were characterized by the observed material balances, their IR and Raman spectra (see the Supporting Information), and their crystal structures. The structures of $[\text{PPh}_4][\text{Ga}(\text{N}_3)_5]$, $[\text{PPh}_4][\text{In}(\text{N}_3)_6]$, and $[\text{PPh}_4][\text{Tl}(\text{N}_3)_6]$ were established by single-crystal X-ray diffraction studies (Figure 2, Figure 3, and the Supporting Information). The crystal structure of $[\text{PPh}_4][\text{Ga}(\text{N}_3)_5]$ ^[26] revealed the presence of well-separated $[\text{PPh}_4]^+$ and $[\text{Ga}(\text{N}_3)_5]^{2-}$ ions. The smallest Ga···N and N···N separations between neighboring anions are 7.9 and 5.6 Å, respectively. The observed geometry of the $[\text{Ga}(\text{N}_3)_5]^{2-}$ anion (Figure 2) is derived from a trigonal-bipyramidal GaN_5 skeleton and is in good general agreement with the propeller-type C_s structure predicted by our calculations. This structure is in good agreement with the ones calculated for $\text{As}(\text{N}_3)_5$,^[6,11] $\text{Sb}(\text{N}_3)_5$,^[6,11] and $[\text{Fe}(\text{N}_3)_5]^{2-}$ ^[29] but contrary to the structure observed for $[\text{Bi}(\text{N}_3)_5]^{2-}$ ^[30] or the one calculated for $[\text{Se}(\text{N}_3)_5]^-$,^[31] for which the free valence electron pair on its central atom becomes sterically active, and also in contrast to the theoretically predicted structures of $\text{Nb}(\text{N}_3)_5$ ^[14] and $\text{Ta}(\text{N}_3)_5$.^[14] While the axial M–N–N bonds in $\text{Nb}(\text{N}_3)_5$ and $\text{Ta}(\text{N}_3)_5$ are almost linear and the M–N distances are essentially the same, the five Ga–N–N bonds in $[\text{Ga}(\text{N}_3)_5]^{2-}$ are strongly bent with angles of about 120° and, as expected from VSEPR arguments,^[32] the axial Ga–N bonds are significantly longer than the equatorial ones.

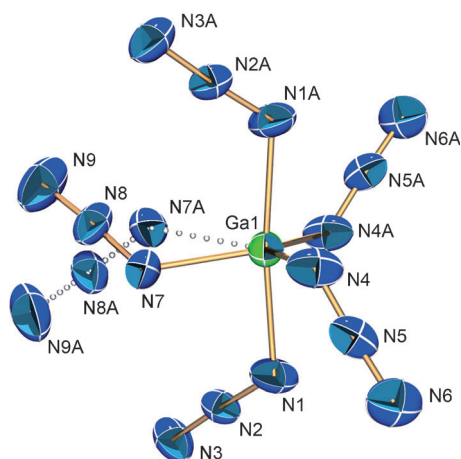


Figure 2. The anion in $[\text{PPh}_4][\text{Ga}(\text{N}_3)_5]$. The two azido groups at N7 and N7A show positional disorder and have site occupancy factors of 0.5. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ga1–N1 2.049(2), Ga1–N4 1.937(2), Ga1–N7 1.948(4), N1–N2 1.191(2), N2–N3 1.152(2); N1–Ga1–N1A 173.42(11), N1–Ga1–N4 89.70(8), N1–Ga1–N4A 87.31(8), N1–Ga1–N7 85.14(14), N1–Ga1–N7A 101.34(14), N4–Ga1–N4A 125.88(13), N4–Ga1–N7 107.11(17), N4–Ga1–N7A 126.38(18).

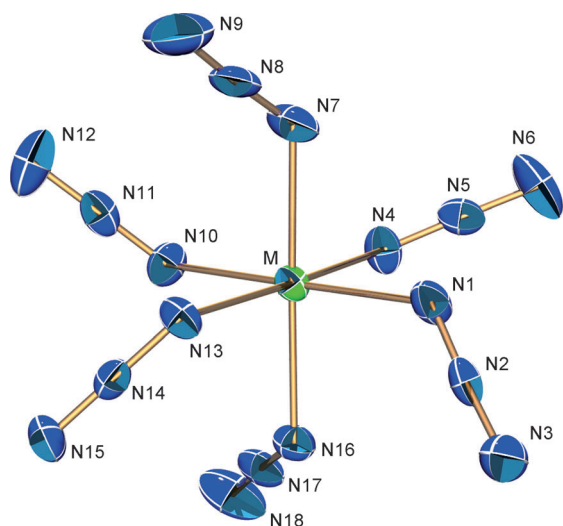


Figure 3. The hexaazido anion in $[\text{PPh}_4][\text{M}(\text{N}_3)_6]$ ($\text{M} = \text{In}, \text{Tl}$). Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°] for $\text{M} = \text{In}$ [$\text{M} = \text{Tl}$]: M–N1 2.217(2) [2.322(3)], M–N4 2.193(2) [2.278(3)], M–N13 2.238(2) [2.328(3)], N1–N2 1.183(3) [1.182(5)], N2–N3 1.160(3) [1.156(5)]; N1–M–N4 90.14(8) [89.61(13)], N1–M–N7 86.27(8) [91.92(14)], N1–M–N10 177.44(8) [176.57(13)], N1–M–N13 93.38(8) [94.51(13)], N1–M–N16 90.27(8) [90.71(13)], N7–M–N16 175.44(8) [174.90(14)].

$[\text{PPh}_4][\text{In}(\text{N}_3)_6]$ crystallizes in the monoclinic space group $P2_1/n$. The X-ray crystal structure^[27] showed the presence of well-separated $[\text{PPh}_4]^+$ cations and $[\text{In}(\text{N}_3)_6]^{3-}$ anions without significant cation–anion interaction. Between neighboring anions, the smallest In···N and N···N separations were found to be 8.4 and 6.4 Å, respectively. $[\text{PPh}_4][\text{Tl}(\text{N}_3)_6]$ crystallizes in the monoclinic space group $P2_1/n$ and is isostructural to

$[\text{PPh}_4][\text{In}(\text{N}_3)_6]$. Again, well-separated cations and anions without significant cation–anion interaction were observed in the X-ray crystal structure.^[28] Between neighboring anions, the smallest Tl···N and N···N interactions were found to be 8.4 and 6.4 Å, respectively. The observed structures of the $[\text{In}(\text{N}_3)_6]^{3-}$ and $[\text{Tl}(\text{N}_3)_6]^{3-}$ anions (Figure 3) are only slightly distorted from perfect S_6 symmetry and are analogous to other hexaazido species such as $[\text{As}(\text{N}_3)_6]^-$,^[6] $[\text{Si}(\text{N}_3)_6]^-$,^[4] $[\text{Ge}(\text{N}_3)_6]^-$,^[3] $[\text{W}(\text{N}_3)_6]^{13} and $[\text{Ti}(\text{N}_3)_6]^{2-}$,^[12] and contrary to that of $[\text{Te}(\text{N}_3)_6]^{2-}$.^[8]$

Theoretical calculations were carried out for all the different polyazido species of this study. For the tetraazido anions $[\text{M}(\text{N}_3)_4]^-$ ($\text{M} = \text{Ga}, \text{In}, \text{Tl}$) (Figure 4 and the Supporting Information), the B3LYP/SBKJ+(d) level of theory

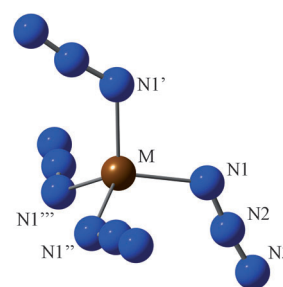


Figure 4. Calculated D_{2d} structure of the tetraazido anions $[\text{M}(\text{N}_3)_4]^-$ ($\text{M} = \text{Ga}, \text{In}, \text{Tl}$). Bond lengths and angles are given in the Supporting Information.

predicts a minimum-energy structure of D_{2d} symmetry. At the MP2/SBKJ+(d) level of theory, the structures of $[\text{Ga}(\text{N}_3)_4]^-$ and $[\text{In}(\text{N}_3)_4]^-$ are predicted to be of D_{2d} symmetry, while the one of $[\text{Tl}(\text{N}_3)_4]^-$ is calculated to be of C_2 symmetry. For the pentaazido anions $[\text{M}(\text{N}_3)_5]^{2-}$ ($\text{M} = \text{Ga}, \text{In}, \text{Tl}$), minimum-energy structures of C_s symmetry were found (see the Supporting Information).

In summary, the extremely shock-sensitive Group 13 triazides $\text{Ga}(\text{N}_3)_3$, $\text{In}(\text{N}_3)_3$, and $\text{Tl}(\text{N}_3)_3$ have been prepared in SO_2 and CH_3CN solutions. The use of the corresponding fluoride starting materials and SO_2 as a solvent provides a convenient synthesis for the neat free triazides and firmly established the existence of thallium triazide. In CH_3CN , the new $\text{M}(\text{N}_3)_3 \cdot \text{CH}_3\text{CN}$ donor–acceptor adducts were obtained. Reactions of the triazides with either stoichiometric amounts or an excess of tetraphenylphosphonium azide in CH_3CN yield exclusively the novel $[\text{Ga}(\text{N}_3)_5]^{2-}$, $[\text{In}(\text{N}_3)_6]^{3-}$, and $[\text{Tl}(\text{N}_3)_6]^{3-}$ anions, the first examples of multiply charged Group 13 polyazido anions. Furthermore, the series $\text{M}(\text{N}_3)_3$, $\text{M}(\text{N}_3)_3 \cdot \text{CH}_3\text{CN}$, $[\text{M}(\text{N}_3)_4]^-$, $[\text{M}(\text{N}_3)_5]^{2-}$, and $[\text{M}(\text{N}_3)_6]^{3-}$ ($\text{M} = \text{Ga}, \text{In}, \text{Tl}$) has been studied by theoretical calculations.

Experimental Section

Caution! The polyazides of this work are extremely shock-sensitive and can explode violently upon the slightest provocation. They should be handled only on a scale of less than 1 mmol using appropriate safety precautions.^[15] In addition, thallium and its compounds are

very poisonous. Ignoring safety precautions can lead to serious injuries!

Materials and apparatus: All reactions were carried out in Teflon-FEP ampules that were closed by stainless steel valves. Volatile materials were handled in a Pyrex glass vacuum line. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glove box. Raman spectra were recorded in the Teflon reactors in the range 4000–80 cm⁻¹ on a Bruker Equinox 55 FT-RA spectrophotometer using a Nd-YAG laser at 1064 nm with power levels less than 50 mW. Infrared spectra were recorded in the range 4000–400 cm⁻¹ on a Midac, M Series FTIR spectrometer using KBr pellets. The pellets were carefully prepared inside the glove box using an Econo minipress (Barnes Engineering Co.). The starting materials GaF₃, InF₃ (both Aldrich), and TiF₃ (Ozark Mahoning) were used without further purification. Me₃SiN₃ (Aldrich) was purified by fractional condensation prior to use. Solvents were dried by standard methods and freshly distilled prior to use. PPh₄N₃ was prepared by a literature method.^[33]

Preparation of M(N₃)₃ (M = Ga, In, Tl): A sample of MF₃ (0.2 mmol) was loaded into a Teflon-FEP ampule. SO₂ (40 mmol) and Me₃SiN₃ (1.0 mmol) were added in vacuo at –196 °C. The mixture was allowed to warm to ambient temperature. After 10 h at ambient temperature, white to orange precipitates were obtained. The temperature was lowered to –20 °C and all volatile material was removed under vacuum. After additional exposure to vacuum for 4 h at ambient temperature, off-white to orange solids were obtained.

Preparation of M(N₃)₃·CH₃CN (M = Ga, In, Tl): A sample of MF₃ (0.40 mmol) was loaded into a Teflon-FEP ampule, and acetonitrile (60 mmol) and Me₃SiN₃ (2.0 mmol) were added in vacuo at –196 °C. The mixture was allowed to warm to ambient temperature. After 6 h at ambient temperature, colorless to orange solutions were obtained. The temperature was lowered to –20 °C, and all volatile material was removed under vacuum. After additional exposure to vacuum for 4 h at ambient temperature, off-white to orange solids were obtained. Masses expected for 0.40 mmol of Ga(N₃)₃·CH₃CN, In(N₃)₃·CH₃CN, and Tl(N₃)₃·CH₃CN: 0.094, 0.113, and 0.148 g; masses found: 0.085, 0.120, and 0.135 g, respectively.

Preparation of [Ga(N₃)₅]²⁻ and [M(N₃)₆]³⁻ (M = In, Tl) salts: Under a stream of dry nitrogen, a stoichiometric amount of PPh₄N₃ (0.60 mmol for [Ga(N₃)₅]²⁻ and 0.9 mmol for [M(N₃)₆]³⁻) was added to a frozen solution of the corresponding triazide (0.30 mmol) in CH₃CN (40 mmol) at –64 °C. The reaction mixture was kept at –25 °C for 30 min, occasionally agitated, and then warmed to ambient temperature. After 30 min, all volatile materials were removed at –20 °C in a dynamic vacuum, leaving behind crystalline solids; masses expected for 0.30 mmol of [PPh₄]₂[Ga(N₃)₅], [PPh₄]₃[In(N₃)₆], and [PPh₄]₃[Tl(N₃)₆]: 0.288, 0.416, and 0.442 g; masses found: 0.280, 0.430, and 0.453 g, respectively.

Theoretical methods: The molecular structures, harmonic vibrational frequencies, and IR and Raman vibrational intensities were calculated using second-order perturbation theory (MP2, also known as MBPT(2))^[34] and also at the DFT level using the B3LYP hybrid functional,^[35a–c] which included the VWN5 correlation functional.^[35d] The Stevens, Basch, Krauss, and Jasien (SBKJ) effective core potentials and the corresponding valence-only basis sets were used.^[36] The SBKJ valence basis sets were augmented with a d-polarization function^[37] and a diffuse s + p shell^[38] on each heavy atom, denoted as SBKJ + (d). Hessians (energy second derivatives) were calculated for the final equilibrium structures to verify them as local minima, that is, having a positive definite Hessian. All calculations were performed by using the electronic structure code GAMESS.^[39]

Received: May 5, 2011

Published online: July 15, 2011

Keywords: azides · electronic structure · group 13 elements · structure elucidation · vibrational spectroscopy

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- [26] Crystal data for $C_{48}H_{40}GaN_{15}P_2$: $M_r = 958.61$, monoclinic, space group $C2/c$, $a = 11.771(4)$, $b = 18.031(6)$, $c = 21.793(7)$ Å, $\alpha = 90$, $\beta = 91.974(5)$, $\gamma = 90^\circ$, $V = 4622(2)$ Å³, $F(000) = 1976$, $\rho_{\text{calcd.}}$ ($Z = 4$) = 1.377 g cm^{-3} , $\mu = 0.717 \text{ mm}^{-1}$, approximate crystal dimensions $0.23 \times 0.15 \times 0.09 \text{ mm}^3$, $\theta = 1.87$ to 27.53° , $\text{MoK}\alpha$ ($\lambda = 0.71073$ Å), $T = 140(2)$ K, 19912 measured data (Bruker 3-circle, SMART APEX CCD with χ -axis fixed at 54.74° , using the SMART V 5.630 program, Bruker AXS: Madison, WI, 2003), of which 5242 ($R_{\text{int}} = 0.0369$) unique. Lorentz and polarization correction (SAINT V 6.45 program, Bruker AXS: Madison, WI, 2003), absorption correction (SADABS program, Bruker AXS: Madison, WI, 2003). Structure solution by direct methods (SHELXTL 6.14, Bruker AXS: Madison, WI, 2003), full-matrix least-squares refinement on F^2 , data to parameters ratio: 16.8:1, final R indices [$I > 2\sigma(I)$]: $R1 = 0.0383$, $wR2 = 0.0889$, R indices (all data): $R1 = 0.0530$, $wR2 = 0.0971$, GOF on $F^2 = 1.029$. CCDC 811062 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [27] Crystal data for $C_{72}H_{60}InN_{18}P_3$: $M_r = 1385.11$, monoclinic, space group $P21/n$, $a = 13.1599(14)$, $b = 22.704(2)$, $c = 22.032(2)$ Å, $\alpha = 90$, $\beta = 96.707(2)$, $\gamma = 90^\circ$, $V = 6537.6(12)$ Å³, $F(000) = 2848$, $\rho_{\text{calcd.}}$ ($Z = 4$) = 1.407 g cm^{-3} , $\mu = 0.494 \text{ mm}^{-1}$, approximate crystal dimensions $0.23 \times 0.16 \times 0.10 \text{ mm}^3$, $\theta = 1.29$ to 27.52° , $\text{MoK}\alpha$ ($\lambda = 0.71073$ Å), $T = 163(2)$ K, 40351 measured data (Bruker 3-circle, SMART APEX CCD with χ -axis fixed at 54.74° , using the SMART V 5.630 program, Bruker AXS: Madison, WI, 2003), of which 14707 ($R_{\text{int}} = 0.0649$) unique. Lorentz and polarization correction (SAINT V 6.45 program, Bruker AXS: Madison, WI, 2003), absorption correction (SADABS program, Bruker AXS: Madison, WI, 2003). Structure solution by Patterson method (SHELXTL 6.14, Bruker AXS: Madison, WI, 2003), full-matrix least-squares refinement on F^2 , data to parameters ratio: 17.4:1, final R indices [$I > 2\sigma(I)$]: $R1 = 0.0382$, $wR2 = 0.0609$, R indices (all data): $R1 = 0.0626$, $wR2 = 0.064$, GOF on $F^2 = 0.892$. CCDC 811063 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [28] Crystal data for $C_{72}H_{60}N_{18}P_3\text{Ti}$: $M_r = 1474.66$, monoclinic, space group $P21/n$, $a = 13.1409(11)$, $b = 22.8133(19)$, $c = 22.0468(19)$ Å, $\alpha = 90$, $\beta = 96.685(2)$, $\gamma = 90^\circ$, $V = 6564.4(10)$ Å³, $F(000) = 2976$, $\rho_{\text{calcd.}}$ ($Z = 4$) = 1.492 g cm^{-3} , $\mu = 2.593 \text{ mm}^{-1}$, approximate crystal dimensions $0.45 \times 0.19 \times 0.18 \text{ mm}^3$, $\theta = 1.29$ to 27.53° , $\text{MoK}\alpha$ ($\lambda = 0.71073$ Å), $T = 142(2)$ K, 40264 measured data (Bruker 3-circle, SMART APEX CCD with χ -axis fixed at 54.74° , using the SMART V 5.630 program, Bruker AXS: Madison, WI, 2003), of which 14611 ($R_{\text{int}} = 0.0305$) unique. Lorentz and polarization correction (SAINT V 6.45 program, Bruker AXS: Madison, WI, 2003), absorption correction (SADABS program, Bruker AXS: Madison, WI, 2003). Structure solution by Patterson method (SHELXTL 6.14, Bruker AXS: Madison, WI, 2003), full-matrix least-squares refinement on F^2 , data to parameters ratio: 17.3:1, final R indices [$I > 2\sigma(I)$]: $R1 = 0.0309$, $wR2 = 0.0729$, R indices (all data): $R1 = 0.0422$, $wR2 = 0.0775$, GOF on $F^2 = 1.050$. CCDC 811064 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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