A Second Polymorphic Form of Trimethylindium: Topology of Supramolecular Architectures of Group 13 Trimethyls

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Crystallization of Me_3In from hexane solution at ambient temperature allows for the isolation of a new phase that cannot be obtained by classical sublimation routes. The crystal structure analysis revealed that this new polymorph of Me_3In crystallizes in the rhombohedral space group $R\bar{3}$. The primary structural effect of the $In-CH_3\cdots In$ intermolecular interactions results in the formation of cyclic hexamers with 12-membered $(InC)_6$ rings of an extended-chair conformation. The shortest intermolecular In⋯C contact is 3.028(4) Å with In⋯H distances between 2.74 and 2.79 Å. The hexamers are further linked by longer $In-CH_3\cdots In$ bridges into the 3D network. In addition, the tetragonal form of Me_3In was redetermined at 100 K. The presented results demonstrate that the impact of both crystallization conditions and the character of intermolecular forces on clustering events is evident. Finally, the network topology of a family of the group 13 trimethyls is analyzed and correlated.

Introduction

The molecular and crystal structures of the homoleptic group 13 alkyls have attracted considerable attention for decades.[1] These studies have revealed a remarkable diversity of bonding types involving Me_3M species in the solid state with an intimate monomeric species for Me_3B,[2] a dimer with two bridging methyl groups for Me_3Al,[3,4] and tetramers with extended supramolecular structures and a relatively weak $M-CH_3\cdots M$ bridge for the heavier analogues.[2,5,6] It is pertinent to note that the long history of studies on the nature of the bridge bonding in Al_2Me_6 is well documented and a central importance of these studies to an understanding of metal–alkyl bonding in general is well recognized.[3,4] Furthermore, very recently Mitzel and co-workers[5] and Parsons et al.[2] revealed the two different crystal structures of Me_3Ga, a tetragonal form with the space group $P4_2/n$ and a monoclinic one with the space group $C2/c$, respectively. The tetragonal phase was obtained by cooling a sample of $GaMe_3$ through its melting point, and the second polymorph was obtained using laser-assisted crystallization devices. The structure of Me_3In was first determined in 1958[7] and then reexamined in 1990.[8] These studies revealed the tetragonal phase (space group $P4_2/n$) of Me_3In, i.e., the structure closely related to that of Me_3Ga[5] and Me_3Tl.[6] In this polymorph of Me_3In, the indium atoms adopt a primary trigonal planar coordination and are weakly coordinated to the methyl group of a neighboring molecule. The Me_3In molecules are associated into tetramers with essentially planar eight-membered rings that are linked by further weaker interactions into the 3D network (Figure 1a). It should be emphasized that the supramolecular structure consists of two mutually exclusive networks that are related by the crystal lattice translation (Figure 1b).

The earliest investigations by Amma and Rundle on the crystal structure of Me_3In have already alluded to the possibility of polymorphism.[7] On the basis of crystal morphology, the authors suggested the presence of a pseudohexagonal (more likely triclinic) form. However, three decades later Blake and Cradock, varying sublimation regimes and after a careful variable-temperature X-ray diffraction study, did not find evidence for any other stable crystalline phase of Me_3In.[8] On the other hand, very recent DFT calculations by Parsons and co-workers were used to draw energetic comparisons between the homoleptic group 13 methyl polymorphs and pointed to the conclusion that “it is quite possible

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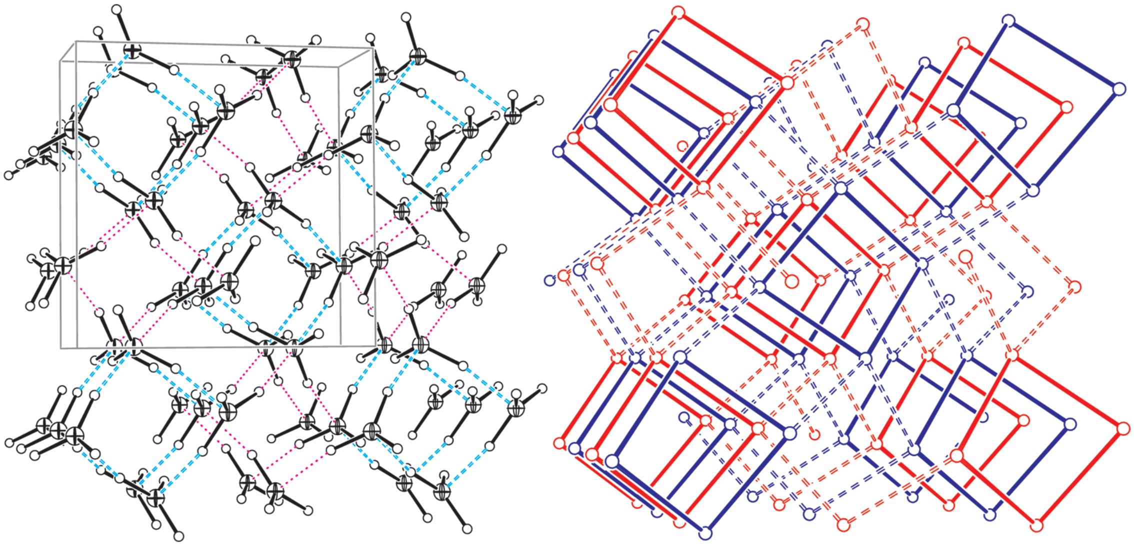

Figure 1. Crystal structure of the tetragonal form of Me_3In viewed along the *c*-axis. Left: view of the crystal packing showing intermolecular In⋯C contacts (H atoms have been omitted for clarity). Right: view of two interpenetrable 3D frameworks formed by Me_3In molecules as pseudo-tetrahedral nodes (Me_3In molecules are represented by indium atoms and the longer In⋯C−In bridges are shown by dashed lines).

that the unstable phase of $InMe_3$ observed by Amma and Rundle had the BMe_3 structure".[2] In the course of our investigation on the structure and reactivity of the homoleptic main group alkyls,[9] we report here the structural characterization of a new stable polymorph of Me_3In isolated from a hexane solution at ambient temperature and discuss the structural similarities and differences between Me_3M polymorphs and their network topology.

Results and Discussion

Isolation and Structure Characterization of a New Polymorph of Me_3In. Trimethylindium was prepared according to the literature procedure[10] and isolated by sublimation, yielding a colorless crystalline solid. The thus prepared crystalline phase of Me_3In (i.e., the tetragonal form as confirmed by the X-ray analysis, vide infra) is freely soluble in noncoordinating solvents, including hexane. However, when a hexane solution of Me_3In was left for a couple of days at ambient temperature, a white crystalline solid deposited, which was isolated by filtration, washed with cold pentane, and dried in a nitrogen flow. The crystals of Me_3In obtained directly by this procedure were found to be suitable for single-crystal X-ray diffraction. The low-temperature X-ray study of this new crystalline material revealed a supramolecular architecture markedly different from that of the tetragonal phase of Me_3In. The new polymorph of Me_3In crystallizes in the rhombohedral space group $R\bar{3}$. The asymmetric unit contains only one molecule and the total number of molecules within the unit cell is 18. As the crystal structure of the tetragonal form was previously determined at room temperature, to obtain more precise geometric parameters and a more valuable data comparison as well as learn more about the influence of intermolecular forces on the crystal structure, we also reexamined the tetragonal form of Me_3In at 100 K. Selected interatomic distances and angles for both polymorphic forms are summarized in Table 1. The salient feature of the low-temperature crystal structure is a remarkable shortening (by ca. 0.15 Å) of the intermolecular $In-CH_3\cdots In$ distances that join the basic tetrameric units, while the In−C covalent bonds and the intermolecular $In-CH_3\cdots In$ distances within the tetramers showed differences ranging from 0.01 to 0.05 Å. This leads to a significant compression of the supramolecular arrangement of Me_3In molecules in the solid state.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Polymorphs of Me_3In

	rhombohedral Me_3In^a	tetragonal Me_3In^b	tetragonal $Me_3In^{8\ b}$
space group	$R\bar{3}$	$P4_2/n$	$P4_2/n$
temperature	100 K	100 K	273 K
In(1)−C(1)	2.156(3)	2.149(5)	2.136(13)
In(1)−C(2)	2.172(3)	2.171(4)	2.179(12)
In(1)−C(3)	2.173(3)	2.172(4)	2.121(14)
In(1)⋯C(2^i)	3.028(3)	3.048(4)	3.083(12)
In(1)⋯C(3^{ii})	3.134(4)	3.409(4)	3.558(15)
C(1)−In(1)−C(2)	122.44(14)	119.65(18)	119.7(5)
C(1)−In(1)−C(3)	120.97(16)	124.05(18)	123.5(5)
C(2)−In(1)-C(3)	116.29(14)	116.24(17)	116.8(5)
In(1)−C(2)⋯In(1^{iii})	168.36(16)	168.14(18)	168.1(6)
In(1)−C(3)⋯In(1^{iv})	165.75(16)	165.82(18)	166.2(6)
C(2^i)⋯In(1)⋯C(3^{ii})	176.63(13)	164.76(11)	165.4(4)

[a] Symmetry codes: (i) $x-y$, x, $1-z$; (ii) $^1/_3-y$, $-^1/_3+x-y$, $-^1/_3+z$; (iii) y, $-x+y$, $1-z$; (iv) $^2/_3-x+y$, $^1/_3-x$, $^1/_3+z$. [b] Symmetry codes: (i) y, $1/2-x$, $1/2-z$; (ii) $1/2+y$, $-x$, $1/2+z$; (iii) $1/2-y$, x, $1/2-z$; (iv) $-y$, $-1/2+x$, $-1/2+z$.

The molecular and crystal structures of the rhombohedral phase of Me_3In are shown in Figure 2. The primary coordination of the metal center in the C_3In skeleton is close to trigonal planar, with the In(1) atom displaced 0.0701(2) Å out of the ligand plane. The In−C distances, on average 2.167 Å, match perfectly the values determined for the tetragonal form at 100 K (2.164 Å). The differentiation of the length of the primary In−C bonds is fully consistent with the involvement of the respective methyl groups in the

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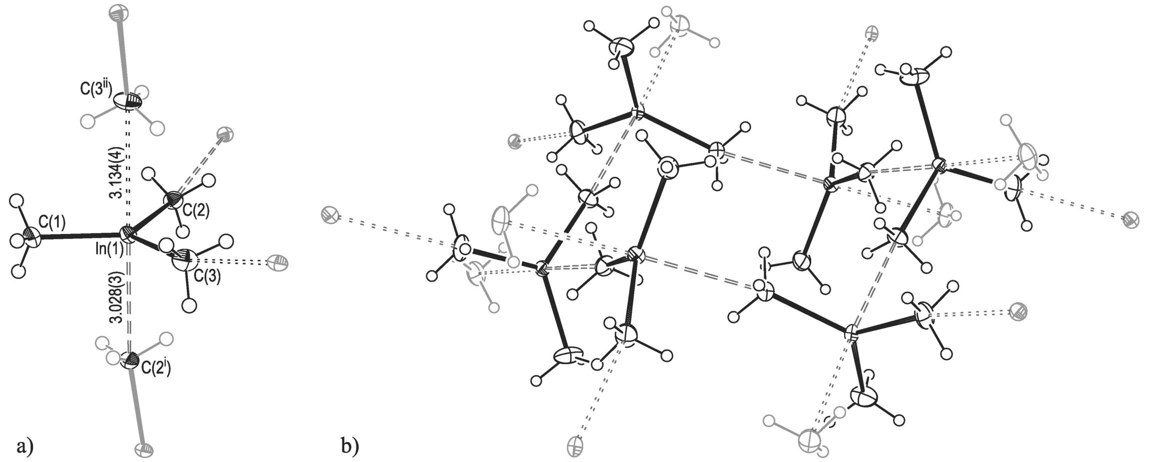

Figure 2. (a) Coordination environment at the metal center in the rhombohedral phase of Me$_3$In (thermal ellipsoids are drawn at 50% probability). The secondary interactions between the indium atom and the methyl groups are illustrated by dashed lines. (b) View of cyclic hexamers formed in the crystal structure. Shorter and longer In⋯C contacts are shown by dashed and dotted lines, respectively.

secondary bonding: the C(1) methyl group is not engaged in any intermolecular interactions and the In(1)−C(1) bond (2.156(3) Å) is the shortest one. As in the tetragonal form, the indium atoms are additionally weakly coordinated to two methyl groups of neighboring molecules. The shortest intermolecular In⋯C contact is 3.028(3) Å for the C(2^{i}) atom, with In⋯H distances between 2.74 and 2.79 Å. The In⋯methyl intermolecular interactions are almost perpendicular to the primary coordination plane with the C(2^{i})⋯In(1)⋯C(3^{ii}) angle of 176.63(13)°. The In−C⋯In angles at the bridging carbon atoms are close to 170°. The primary structural effect of these In−CH$_3$⋯In intermolecular interactions is the formation of cyclic hexamers with 12-membered (InC)$_6$ rings and an extended-chair conformation (Figure 2b). All the Me$_3$In molecules in a hexamer are related by the crystallographic 3-fold inversion axis $\bar{3}$. The closest In⋯In distance within a hexamer is 5.175(1) Å, while the transannular In⋯In separation equals 9.635(1) Å. The hexamers are further connected by the longer In−CH$_3$⋯In bridges [e.g., with the In(1)⋯C(3^{ii}) distance of 3.134(4) Å and In(1)⋯H distances of about 2.84 Å] into a 3D network (Figures 2 and 3). These interactions result in the formation of secondary eight-membered (InC)$_4$ and 12-membered (InC)$_6$ rings in both of which indium atoms are almost coplanar. The rings stack along the crystallographic *c*-axis in an eclipsed fashion to give channels of 3-fold symmetry with a diameter of about 5 Å (14% of the crystal volume).

Thus, the tetragonal and rhombohedral phases of Me$_3$In differ qualitatively from the two others by the size and the shape of the secondary building unit; that is, the molecules are arranged into essentially planar tetramers or into hexamers with an extended-chair conformation, respectively. The interconnections between these subunits are elongated. In both Me$_3$In polymorphs, the overall coordination at the indium atom may be described as trigonal bipyramidal, with the primary In−C bonds in the equatorial plane (Figure 2a). However, in the tetragonal structure the coordination sphere of the indium atom is less symmetrical, and the secondary interactions are weaker and clearly diversified, as manifested by the lengths of In⋯C contacts forming the tetramers and those between the tetramers, 3.048(4) and 3.409(4) Å, respectively (Table 1). It should also be noted that the supramolecular arrangement of

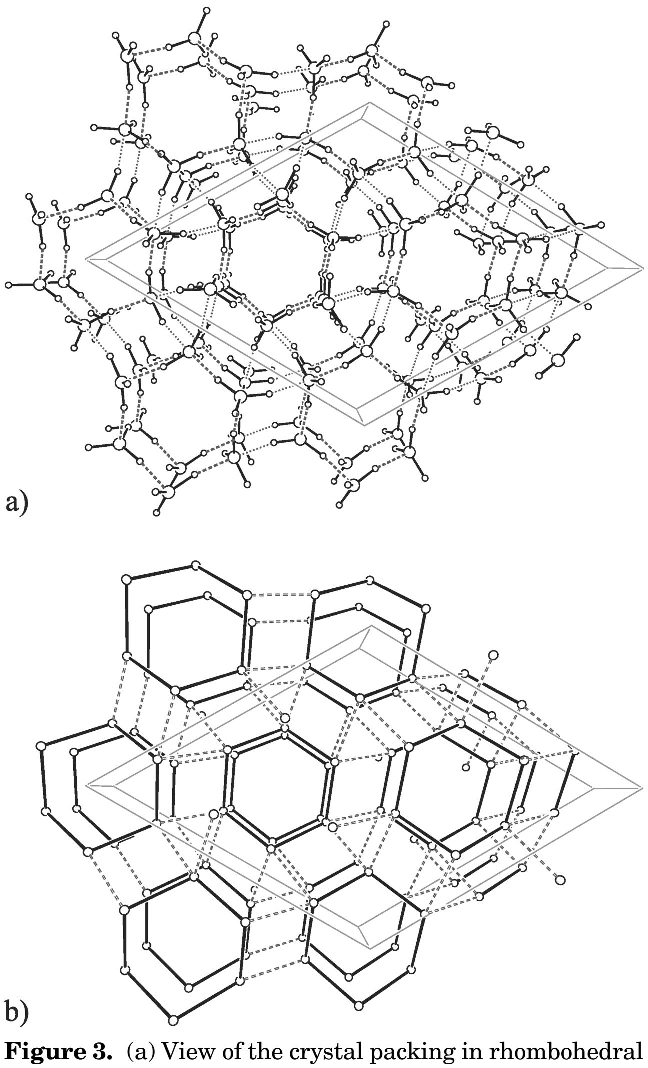

Figure 3. (a) View of the crystal packing in rhombohedral Me$_3$In along the hexagonal *c*-axis showing intermolecular In⋯C contacts (dashed and dotted lines). (b) View of the 3D network formed by Me$_3$In molecules as pseudo-tetrahedral nodes (Me$_3$In molecules are represented by indium atoms and the longer In⋯C−In bridges are shown by dashed lines).

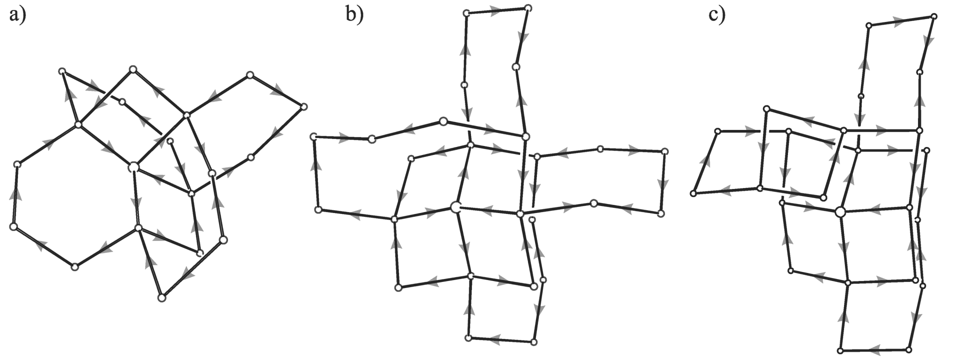

Figure 4. View of the fragments of 4-connected 3D frameworks generated in three structural types of Me_3M (M = Ga, In, Tl) showing the shortest rings contained in each angle of a vertex and the directionality of edges (donor→acceptor): (a) rhombohedral polymorph of Me_3In, vertex symbol (4·4·6·6·6·6); (b) tetragonal form of Me_3M (M = Ga, In, and Ta), vertex symbol (4·4·4·8_2·8·8); (c) monoclinic Me_3Ga, vertex symbol (4·4·4·8·8·10_2) (for the second, crystallographically independent molecule the arrows in the framework should be oppositely directed).

Me_3In molecules in the solid state leads to a rather loosely packed crystal structure; according to crystallographic data, the density of the rhombohedral phase at 100 K [$\rho(100\ K) = 1.743\ g\cdot cm^{-3}$] is 12.4% lower than that of the tetragonal form [$\rho(100\ K) = 1.989\ g\cdot cm^{-3}$].

Topology of the Group 13 Me_3M Supramolecular Architectures. Each Me_3M (M = Ga, In, and Tl) molecule in the identified polymorphic forms is connected via secondary interactions with four molecules, using the two acceptor sites in the axial positions and the two equatorial donor sites (the third equatorial methyl group acts always as a spectator) (cf. Figure 2a). From the topological point of view, Me_3M molecular units in the 3D network can be reduced to the simple 4-connected node represented by the metal center. Such approach leads to the net of the rhombohedral Me_3In form, as shown schematically in Figure 3b. In this case, the linear connections between vertexes are equal to 5.175(1) and 5.268(1) Å and correspond to the $In-CH_3\cdots In$ bridges. The 3D framework can be topologically classified as a simple uninodal 4-connected network, each vertex (point) being connected to exactly four neighbors and all vertexes being equivalent (uninodal net). To understand this topology, it is informative to consider the net shown in Figure 4a. A 4-connected net contains six angles defined by pairs of edges, and the connectivity mode can be described by the commonly used long vertex symbol indicating the size and the number of the shortest ring contained in each angle of a vertex.[11]

Figure 4a shows a 3D (4·4·6·6·6·6) topology, in which the 4-connected node is shared by two tetragons and four hexagons. It should be noticed that the connections between nodes ($M-CH_3\cdots M$) have an element of directionality because they link clearly distinguishable donor and acceptor sites; that is why in Figure 4 the edges of nets are designated by arrows showing the direction from the donor to the acceptor. Hence, owing to the directional aspect of the methyl bridges, both tetragonal rings and one chairlike hexagonal ring have a circulatory character, while the remaining planar hexagonal rings are noncirculatory. The tetragonal rings should be circulatory in character due to the geometrical restraints introduced by the geometry of the indium coordination sphere and by the almost linear methyl bridges.

As 4-connected networks play an important role in inorganic structural chemistry, a considerable effort has been spent on enumerating possible structures and characterizing their topologies.[12] Systematic enumeration is particularly useful in the study of zeolites, for which 161 structural types have been identified.[13] A new approach to the problem of systematic enumeration of 4-connected networks (based on advances in mathematical tiling theory) was recently reported by Klinowski and co-workers.[14] The application of those results to the analysis of the 3D framework in the rhombohedral polymorph of Me_3In shows the structure to be topologically equivalent to the well-known sodalite type structure (SOD), i.e., the network of the tetrahedral Si and Al atoms in the mineral sodalite (ideal formula $Na_4Al_3Si_3O_{12}Cl$). This topology occurs for an enormous number of compounds including oxides, sulfides, nitrides, halides, clathrate hydrates, and intermetallic phases. Structural motifs characteristic of the ideal high-symmetry sodalite network are cages with the shape of a truncated octahedron having $m\bar{3}m$ point symmetry, while the vertex site symmetry is $\bar{4}m2$ and the whole crystal network has symmetry $Im\bar{3}m$ (Figure 5). The corresponding cage in rhombohedral Me_3In is highly distorted because of the different symmetry of vertexes arising from the overall TBP coordination at the indium atom and the directionality of edges (Figure 5c). The distortion of this cage consists largely of a considerable flattening along the $\bar{3}$ axis (hexagonal *c*-axis). One can easily recognize that the introduction of the edge directionality alone into the original sodalite network causes breaking of the symmetry of both the cage and the corresponding crystal network. Taking into account the forced circulatory character of all tetragonal faces, it can be shown that the conservation of translational

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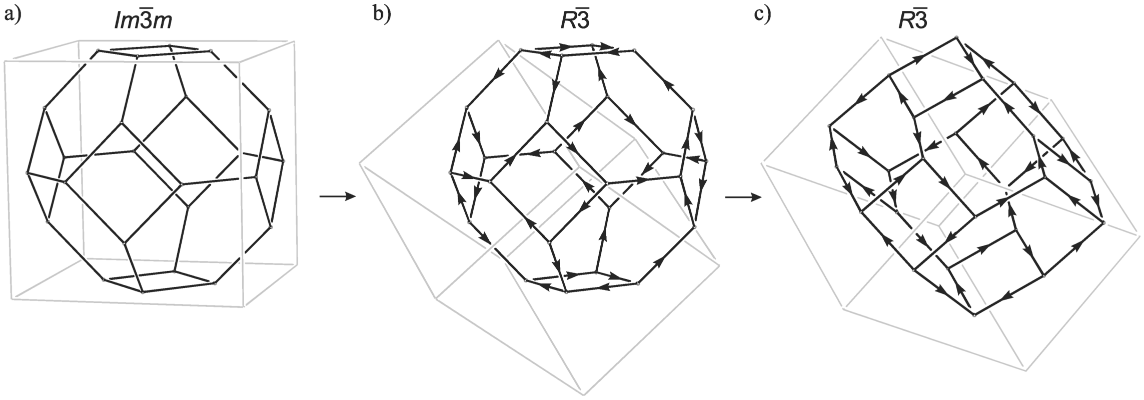

Figure 5. Schematic representation of the symmetry breaking of the sodalite network: (a) truncated octahedron in a cubic sodalite network; (b) sodalite cage after introduction of a circulatory character of edges; (c) highly distorted sodalite-like cage in Me_3In (a unit cell with rhombohedral axes).

symmetry of the original body-centered lattice leads to the rhombohedral space group $R\bar{3}$ (subgroup of $Im\bar{3}m$), as depicted in Figure 5b. Thus, the resulting cage is characterized by lower symmetry (the $\bar{3}$ point group, subgroup of the $m\bar{3}m$ group) and strictly corresponds with the oblate cage existing in rhombohedral Me_3In (Figure 5c).

In general, one can expect that other supramolecular frameworks exhibit analogous relations to the parent, high-symmetry structure in which the details of the symmetry breaking (due to the linkage directionality) are different but are in accordance with the well-known relations between space groups. A relevant example is provided by the extensive series of highly symmetrical guanidinium-templated metal carbonates reported recently by Robson et al.[15] All of these compounds form carbonate-bridged networks with the sodalite topology. Structures fall into two classes depending on the nature of the carbonate bridges in the framework. The first type, comprising structures with symmetric bridges (monodentate−monodentate CO_3^{2-} ligands), has the highest $Im\bar{3}m$ symmetry, while in the second type, due to directed bridges (bidentate−monodentate ligands), the symmetry is lowered to the $Fd\bar{3}c$ space group (subgroup of $Im\bar{3}m$ with cell edges twice that of the first type). The observed symmetry relations indicate that the analysis of the symmetry of known frameworks with regard to the directionality of linkages can be a helpful tool in the prediction and classification of supramolecular structures.

On the other hand, the topology of both mutually exclusive supramolecular networks occurring in the tetragonal form of Me_3M (M = Ga, In, and Tl) may be described as the 3D ($4{\cdot}4{\cdot}4{\cdot}8_2{\cdot}8{\cdot}8$) network (Figure 4b) and corresponds to the GIS framework type (gismondine). Furthermore, in the third structural type of the homoleptic group 13 methyl compounds, represented by the monoclinic polymorph of Me_3Ga, the molecules form, as far as we know, the unprecedented 3D ($4{\cdot}4{\cdot}4{\cdot}8{\cdot}8{\cdot}10_2$) topology (Figure 4c). It should be emphasized that the structure contains two crystallographically independent molecules of Me_3Ga with the same vertex symbol, but with reversed direction of linkages (edges).

Concluding Remarks. In this report we have described the structural study on a new stable rhombohedral polymorph of Me_3In that has been isolated by crystallization from hexane solution at ambient temperature. We have shown that, as in the other polymorphs of the group 13 trimethyl derivatives, the weak intermolecular metal-to-methyl interactions play a crucial role in the molecular assembly of the crystalline solid. In the case of the rhombohedral form of Me_3In, the primary structural effect of the $In-CH_3\cdots In$ intermolecular interactions is the formation of cyclic hexamers with 12-membered $(InC)_6$ rings of an extended-chair conformation. The hexamers are further connected by the longer $In-CH_3\cdots In$ bridges into the 3D network. The orientation of four binding sites of a Me_3In molecule (one methyl group is not engaged in any intermolecular interaction) gives rise to a rather unusual node geometry, but the topology of the network is equivalent to that observed in the mineral sodalite, where the tetrahedral units (SiO_4 or AlO_4) are linked together by oxygen bridges. On the other hand, in the tetragonal phases of Me_3In (isolated by sublimation) or Me_3Ga and Me_3Tl, the molecules are associated into cyclic tetramers which are further assembled into a 3D network of the topology corresponding to the gismondine framework. Thus, the topologically equivalent arrangement may be generated despite the fact that the shape and directions of intermolecular bridges between molecular building blocks differ significantly, and this observation should be valuable in regard to geometric design principles for the construction of 4-connected networks from various building units.

Polymorphism is a major challenge to the fundamental understanding of crystallization. The reported results provide additional evidence for the impact of both the crystallization condition and the character of intermolecular forces on clustering events. The mode of assembly of Me_3M molecules in crystals is strongly influenced by the nature of the intermolecular interactions. In the case of Me_3B, these include primarily van der Waals forces, while for the heavier group 13 metal analogues, electrostatic or agostic interactions in an extended fashion are involved.[5] Since these forces are relatively weak, and there is a delicate balance and competition between directional noncovalent interactions and nondirectional noncovalent interaction (such as van der Waals packing forces), one may expect a high

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Table 2. Crystal Data, Data Collection, Structure Solution, and Refinement Parameters for Rhombohedral and Tetragonal Me_3In.

	rhombohedral Me_3In	tetragonal Me_3In
formula	C_3H_9In	C_3H_9In
fw	159.92	159.92
cryst size, mm	0.24 × 0.14 × 0.14	0.45 × 0.32 × 0.25
cryst syst	trigonal	tetragonal
space group, no.	$R\bar{3}$, 148	$P4_2/n$, 86
temperature, K	100(2)	100(2)
a, Å	22.1954(6)	13.0454(2)
b, Å	22.1954(6)	13.0454(2)
c, Å	6.4285(2)	6.27780(10)
α, deg	90	90
β, deg	90	90
γ, deg	120	90
V, $Å^3$	2742.62(14)	1068.37(3)
Z	18	8
D_{calc}, g cm^{-3}	1.743	1.988
$F(000)$	1368	608
radiation used	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
μ, mm^{-1}	3.721	4.246
θ range, deg	3.3−27.5	3.9−27.5
no. of reflns collected	14 137	17 135
no. of unique data, R_{int}	1397, 0.090	1215, 0.047
no. of obsd data [$I > 2\sigma(I)$]	1367	1169
no. of data/param/restrnts	1397/41/0	1215/41/0
goof on F^2	1.165	1.301
R1, wR2 (all data)[a]	0.0245, 0.0568	0.0316, 0.0725
R1, wR2 (obsd data)[a]	0.0235, 0.0564	0.0299, 0.0718
weights a, b[b]	0.0110, 18.46	0.0209, 3.63
largest resids, e·$Å^{-3}$	+0.87, −0.73	+0.87, −0.48

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$. [b] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

propensity of Me_3M compounds toward polymorphic structures. Therefore, it is likely that new network topologies for this group of homoleptic species will be found in the near future. Constraints imposed by the five-coordinate metal environment and the preferred geometry of the methyl bridge confine the scope of chemically feasible structures. There are some compounds that can be used to model hypothetical polymorphs. For example, boron trifluoride forms in the solid state a 3D network through the intermolecular B−F···B bridges and the boron atoms show a total coordination number of five with nearly trigonal bipyramidal geometry.[16,17] An analysis of the network shows that the 3D structure is equivalent to the well-known ABW zeolite type ($4{\cdot}6{\cdot}4{\cdot}6{\cdot}6{\cdot}8_2$) and may be a starting point to predict new polymorphs of the group 13 trimethyl derivatives using a computational chemistry approach.

Experimental Section

General Comments. All operations were carried out under dry nitrogen using standard Schlenk techniques. Solvents and reagents were purified and dried by standard techniques.

Crystallographic Studies. Single crystals of rhombohedral and tetragonal polymorphs of Me_3In suitable for X-ray diffraction studies were placed in thin walled capillary tubes (Lindemann glass) in an inert atmosphere, plugged with grease and flame sealed. X-ray diffraction data were collected on a Nonius Kappa-CCD diffractometer. Crystal data, data collection, and refinement parameters for both polymorphs are given in Table 2. The data sets were corrected for Lorentz−polarization effects. In the case of the tetragonal crystal an empirical absorption correction was performed using the Scalepack program.[18] For the rhombohedral Me_3In the intensities were corrected for absorption anisotropy by the method published by Blessing[19] and implemented in the Platon package.[20] The structures were solved by direct methods using the SHELXS-97 program[21] and refined by the full-matrix least-squares method against F^2 values (SHELXL-97[22]). All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically idealized coordinates and allowed to ride on their parent C atoms with a fixed isotropic displacement parameter equal to 1.5 times the value of the equivalent isotropic displacement parameter of the parent carbon. The final Fourier-difference maps have no significant chemical meaning. ORTEP drawings were made using Ortep3 for Windows.[23]

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Supporting Information Available: Crystallographic information file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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