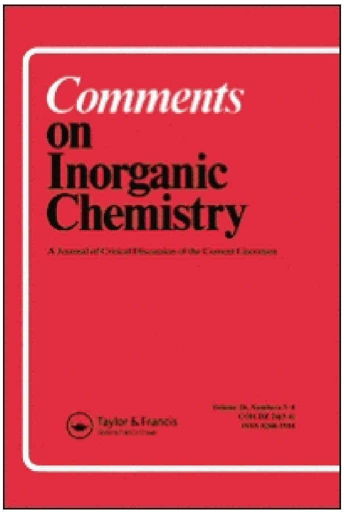

Comments on Inorganic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Oxide, Chalcogenide and Related Clusters of Aluminum, Gallium and Indium

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To cite this Article Barron, Andrew R.(1993) 'Oxide, Chalcogenide and Related Clusters of Aluminum, Gallium and Indium', Comments on Inorganic Chemistry, 14: 2, 123 — 153

To link to this Article: DOI: 10.1080/02603599308048659

URL: http://dx.doi.org/10.1080/02603599308048659

Oxide, Chalcogenide and Related Clusters of Aluminum, Gallium and Indium

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Received July 20, 1992

A review of the cluster compounds of the group III metals (aluminum, gallium, and indium) with group VI donor atoms, focusing on recent developments in the author's laboratory, is given. Compounds with oxide, and related hydroxide, alkoxide and siloxide ligands, are discussed with relevance to the Kaminsky co-catalyst (methylalumoxane), and the sol-gel synthesis of group III oxide ceramics, respectively. The sulfide clusters $[(^tBu)GaS]_x$ undergo a facile topological rearrangement between the different oligomers (i.e., $x = 4, 6, 7,$ and 8), while the cubane cluster $[(^tBu)GaS]_4$ provides the first evidence that new metastable phases of binary compounds may be deposited by chemical vapor deposition from a predesigned molecular motif. The structural relevance of the group II/VI clusters to solid state materials is also discussed.

Key Words: *aluminum, gallium, indium, oxide, chalcogenide, sulfide, selenide, telluride, cluster*

1. INTRODUCTION

With a combined annual production of over 30 million tons, the oxides and hydroxides of aluminum are undoubtedly among the

Comments Inorg. Chem.
1993, Vol. 14, Nos. 2 & 3, pp. 123–153
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most industrially important chemicals.[1] It is therefore unsurprising that much research has been focused on developing and understanding new methods for the preparation of these materials. A common route to all of the aluminum oxides and hydroxides is via alumina gels. Sometimes referred to as gelatinous alumina, these are two phase systems in which colloidal aluminum hydroxide, or an oxide hydroxide based material, is the predominant solid phase, the second phase being water, an organic solvent, or both. Gelatinous aluminas have traditionally been prepared by the neutralization of a concentrated aluminum salt solution.[2] However, the strong interaction of the freshly precipitated alumina gels with ions from the precursor solution makes it difficult to prepare the gels in pure form.[3] To avoid this complication alumina gels may be prepared from the hydrolysis of aluminum alkoxides, $[Al(OR)_3]_x$. Although this method was originally reported by Adkins in 1922,[4] it was not until the 1970's when Teichmer and co-workers[5] reported the preparation of alumina aerogels, and Yoldas[6] showed that transparent ceramic bodies can be obtained by the pyrolysis of suitable alumina gels, that interest increased significantly. In addition to the formation of alumina bodies from the pyrolysis of gels prepared by the hydrolysis of aluminum alkoxides (Eq. (1)) Yoldas demonstrated that aluminum silicate ceramics, $(Al_2O_3)_x(SiO_2)_y$, could also be prepared using related methodology (Eq. (2)).[7]

$$Al(OR)_3 \xrightarrow{H_2O} \text{Al-gel} \xrightarrow{\Delta} Al_2O_3 \qquad (1)$$

$$Al(OSiR_3)_3 \xrightarrow{H_2O} \text{Al-Si-gel} \xrightarrow{\Delta} (Al_2O_3)_x(SiO_2)_y \qquad (2)$$

The aluminum–silicon based gels formed on the hydrolysis of aluminum siloxides (Eq. (2)) are clearly related to the siloxy substituted aluminum based polymer or alumoxanes,[8] first reported in 1958 by Andrianov (Eq. (3)),[9] suggesting that the "alumina gels" prepared from aluminum alkoxides and siloxides are not colloidal aluminum hydroxides, or oxide hydroxides, but alumoxanes, i.e., organically substituted aluminum oxygen macromolecules.

$$n/2 + 1\ [\mathrm{Al(OSiR_3)_3}]_2 + n + 1\ \mathrm{H_2O} \rightarrow \mathrm{(R_3SiO)_2AlO[Al(OSiR_3)O]_{\mathit{n}}Al(OSiR_3)_2} \quad (3)$$

In contrast to the purposeful hydrolysis of group III inorganic coordination compounds, chemists handling organometallic reagents have made every effort to limit hydrolytic decomposition, carrying out reactions with scrupulously dried solvents and glassware, since the reaction with water is often extremely exothermic. However, under controlled conditions it is possible to obtain some of the intermediates in the complete hydrolysis to the metal hydroxide. The hydroxide and oxide compounds formed are of interest not only in the context of the hydrolysis reaction *per se*, but also because of the use of certain alkyl derivatives as co-catalysts in the Ziegler–Natta polymerization of olefins.[10] In this regard much recent concern has been focused upon the product from the hydrolysis of $\mathrm{AlMe_3}$, methylalumoxane (MAO).[11]

Unlike the more widely studied transition metal oxo and hydroxo compounds, there is little structural data available on the hydrolysis products of group III compounds. However, those that have been isolated and characterized have been found to be 3-dimensional clusters, not linear chains or cyclic rings as is so often depicted in the literature.[11]

Recent work in our laboratory has been focused on the structural elucidation of the path from small molecules to solid state materials, and as part of this study we have become interested in the cluster chemistry of the group III elements with group VI donor ligands.

The chalcogenide analogs of the group III oxo- and hydroxo-clusters have received minimal attention, most probably since no commercial application has prompted funding of their study! However, given their homologous relationship to the oxygen donor chemistry they have received increasing academic interest, which has in turn led to the possible commercial application of some compounds as precursors for new phases of solid state materials. The connection between III/VI molecular clusters and their related non-molecular solids is discussed, with reference to molecules mimicking the solid state, and the solid state being controlled by the structure of molecular precursors.

2. OXIDES AND OXYGEN DONOR LIGANDS

Hydrolysis of Inorganic Compounds

Due to its industrial importance the hydrolysis of aluminum salts has been extensively studied for well over a century,[12] and several polyatomic species have been postulated, e.g., $[Al_3(OH)_4]^{5+}$ (potentiometric studies),[13] $[Al_3(OH)_8]^{+}$ (NMR spectroscopy),[14] and $[Al_8(OH)_{20}(H_2O)_x]^{4+}$ (NMR spectroscopy).[15] However, only one, the tridecamer $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, has been isolated and crystallographically characterized.[16]

The structure of $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ is shown in Fig. 1,

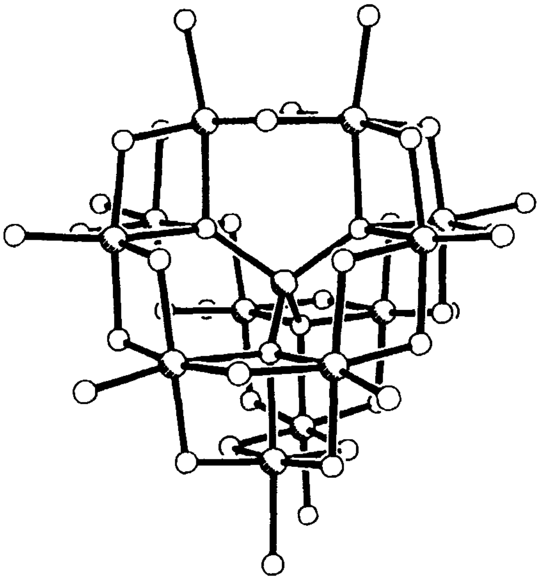
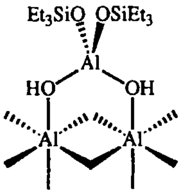


FIGURE 1 The structure of $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$. The aluminum atoms are represented as shaded spheres, and all hydrogen atoms are omitted for clarity.

and consists of twelve AlO_6-octahedra joined by means of common edges. At the center of the cluster is a 4-coordinated tetrahedral aluminum. It is interesting that the groups of three octahedra that, linked by common edges and corners, build up the diaspore and boehmite structures, $[Al(O)(OH)]_n$, can be seen in the $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ cluster. A recent ^{71}Ga NMR spectral study has indicated the formation of the unstable cationic cluster, $[Ga_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, whose structure is proposed to be identical to that of the aluminum analog; however, to date no structural studies has provided verification.[17] Despite the similarity between the tridecamer's structure and that of the minerals boehmite and diaspore, it wasn't until recently that the analogy between minerals and molecules was extended to other aluminum–oxygen macromolecules.[18]

Hydrolytically stable alumoxanes, $[Al(O)(OH)_x(OSiEt_3)_{1-x}]_n$, prepared by both solid state and solution hydrolysis of $[Al(OSiEt_3)_3]_2$, have been shown to have a high hydroxide content ($0.81 < x < 0.85$).[20] On the basis of an extensive multinuclear NMR spectroscopic investigation of these alumoxanes materials a structural model was proposed[20] in which a six-coordinate aluminum/oxygen core, analogous to that found in the minerals boehmite and diaspore, $[Al(O)(OH)]_n$, is encapsulated by end/edge groups consisting of four coordinate aluminum atoms within a six-membered ring (**I**). It is on these four coordinate aluminum centers that the unhydrolyzed Et_3SiO substituents are located.



(I)

Confirmation of this proposed model was obtained by the isolation and X-ray crystallographic structural characterization of the deca-aluminum cluster $Al_{10}(OH)_{16}(OSiEt_3)_{14}$, prepared from the thermolytic disproportionation of the alumoxane formed from the reaction of $[Al(OSiEt_3)_3]_2$ with 0.25 molar equivalents of H_2O (Eq. (4)).[20]

$$Al(OSiEt_3)_3 \xrightarrow{1/4\ H_2O} Al_4(O)(OSiEt_3)_{10} \xrightarrow[-Al(OSiEt_3)_3]{\Delta} Al_{10}(OH)_{16}(OSiEt_3)_{14} \quad (4)$$

The molecular structure of $Al_{10}(OH)_{16}(OSiEt_3)_{14}$ is shown in Fig. 2, and consists of four chemically distinct aluminum environments (two six-coordinate and two four coordinate), five hydroxide environments and two triethylsiloxide environments. The Al_4O_6 core contains four six-coordinate atoms joined by two μ_3- and four μ_2-hydroxide groups and is best considered to consist of two face-shared aluminum-oxygen cubes in which two of the diagonally opposing aluminum vertices are absent. It should be noted

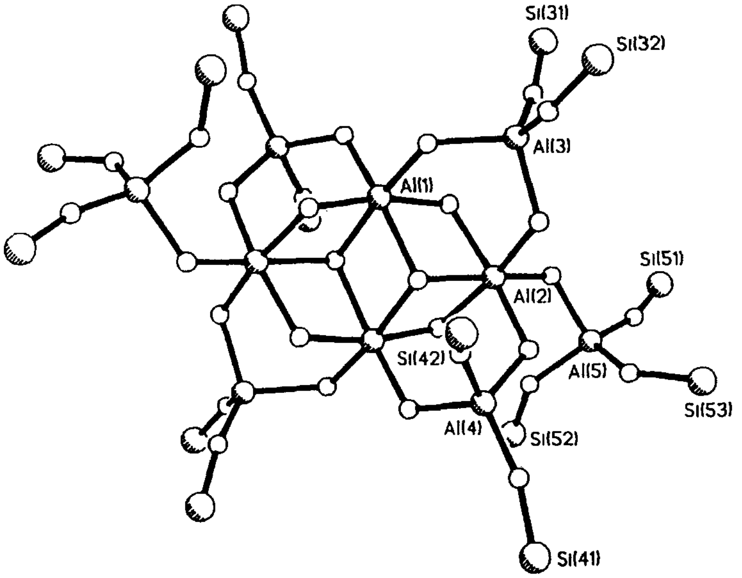


FIGURE 2 The molecular structure of $Al_{10}(OH)_{16}(OSiEt_3)_{14}$. All carbon and hydrogen atoms have been omitted for clarity.

that this core is also the smallest fragment of either boehmite and diaspore that retains their structure. Thus, $Al_{10}(OH)_{16}(OSiEt_3)_{14}$ may be considered as the "missing-link" between simple oligomeric aluminum alkoxides and siloxides, and macroscopic aluminum minerals.

The limited studies reported for gallium compounds indicate them to be structurally similar to those of aluminum,[19] while studies on the hydrolysis of indium compounds show them to be structurally distinct. Potentiometric titration studies of indium (III) nitrate have inferred the existence of cationic clusters, $[In_n \cdot (OH)_n]^{2n+1}$.[19] The best fit of the observed data was proposed to be the tetramer, i.e., $n = 4$.[21] Although a cluster of this general formula has been isolated (see below) it was not from aqueous solution, instead Wieghardt *et al.*[20] reported that basic (NaOH) hydrolysis of indium (III) halides in the presence of 1,4,7-triazacyclonane, L (**II**), yielded the tetranuclear hexacation $[L_4In_4(\mu\text{-}OH)_6]^{6+}$, whose structure is shown in Fig. 3.

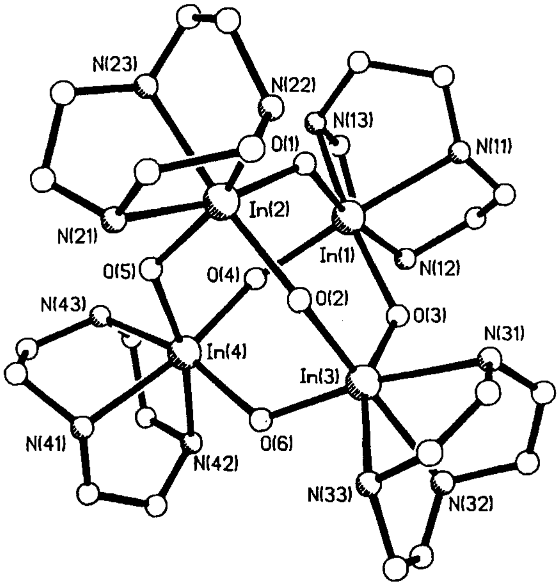
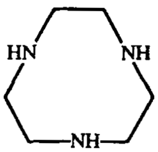


FIGURE 3 Structure of the cation $[L_4In_4(\mu\text{-}OH)_6]^{6+}$ (L = 1,4,7-triazacyclonane).



(II)

The $In_4(\mu\text{-}OH)_6$ core of the cation $[L_4In_4(\mu\text{-}OH)_6]^{6+}$ has an adamantane-like skeleton, with the In atom occupying the corners of a nearly regular tetrahedron, and the μ-OH bridges are located above the centers of the six edges of this tetrahedron.

While the hydrolysis of gallium and indium alkoxides has been essentially ignored with regard to practical applications, Bradley, Hursthouse and co-workers have reported[21] the crystal structure of the penta-indium-oxo-alkoxide cluster, $[(InO^iPr)_5(\mu_2\text{-}O^iPr)_4(\mu_3\text{-}O^iPr)_4(\mu_5\text{-}O)]$, conceptually formed as a result of the partial hydrolysis of $In(O^iPr)_3$. It should be noted, however, that the authors indicate that the penta-indium cluster was prepared in 44% yield, from the reaction of partially hydrolyzed $InCl_3$ and NaO^iPr, in HO^iPr solution. The In_5O_{14} core structure of $[(InO^iPr)_5(\mu_2\text{-}O^iPr)_4(\mu_3\text{-}O^iPr)_4(\mu_5\text{-}O)]$, shown in Fig. 4, consists of an oxo-centered square pyramid of indium atoms, bridged by four μ_2-alkoxo groups

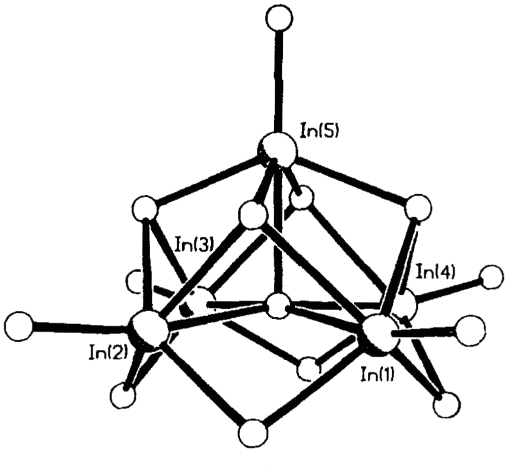


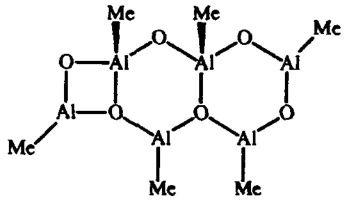
FIGURE 4 The molecular structure of $[(InO^iPr)_5(\mu_2\text{-}O^iPr)_4(\mu_3\text{-}Pr)_4(\mu_5\text{-}O)]$.

around the equator and four μ_3-alkoxo groups on the triangular faces of the indium pyramid. Each of the indium atoms is in a highly distorted octahedral geometry. The low temperature ($-30°C$) ^1H NMR spectrum indicates that the structure observed in the solid state is retained in solution, however, at higher temperatures the μ_2- and μ_3-alkoxo groups undergo facile exchange, for which a $\Delta G^\ddagger$ was estimated to be in the range 43–49 $kJmol^{-1}$.

Hydrolysis of Organometallic Compounds

Alkylalumoxanes, the products from the hydrolysis of aluminum alkyls, were extensively studied in the 1960's as active catalysts in the polymerization of propylene oxide,[22] monosubstituted epoxides,[23] acetaldehyde,[24,25] butadiene,[26] propylene and isobutylene.[27] Recent interest in alumoxanes has arisen primarily from the work of Kaminsky and co-workers who have applied methylalumoxane, (MAO) as a component of a highly active catalyst system for the polymerization of ethylene and propylene.[10] Subsequently Zambelli and co-workers[28] have shown that MAO and $Ti(CH_2Ph)_4$ are catalysts for the preparation of syndiotactic polystyrene, while Catellani *et al.*[29] have used MAO in concert with $Ti(OBu)_4$ as a catalyst for polyacetylene film synthesis.

On the basis of the known structure of dialkysiloxane polymers, alkyl alumoxanes were originally proposed to have a linear chain structure consisting of alternate aluminum and oxygen atoms.[11] Such a structure would obviously require the aluminum to have a coordination number of three, which is rare, only existing in compounds in which oligomerization is hindered by sterically bulky ligands. Since it is common for aluminum to maximize its coordination number through the formation of dimers and trimers through bridging ligands, the majority of workers have since proposed that the aluminum has a coordination number of four.[11] The first crystallographic evidence for this was provided by Atwood *et al.*,[30] with their structural determination of the $[Al_7O_6Me_{16}]^-$ anion. The anion consists of an Al_6O_6 ring capped by a seventh aluminum atom that is bonded to three alternate oxygen atoms in the ring. The similarity of this structure to those of dimeric and trimeric alkoxide compounds of aluminum has prompted many groups to propose structures based on either fused four- or six-membered rings or both (e.g., **III**).[11]



(III)

Although these models do appear to be reasonable since they more closely follow known aluminum chemistry, significant problems remain, namely that while the core aluminum centers are coordinatively saturated, the periphery remains three coordinate. Various proposals based on either alkyl bridges and/or additional trialkyl aluminum groups have, therefore, been forwarded. However, recent work[31] has shown for the first time that alkyl alumoxanes, like their hydroxy and siloxy companions (above), have a 3-dimensional structure, comparable, not to a dense mineral structure but to the open cage structure of the well-characterized iminioalanes, $[RAlNR']_n$.

The hydrolysis of $Al(^tBu)_3$ yields the trimeric hydroxide whose structure has been confirmed by X-ray crystallography (Eq. (5)).

$$Al(^tBu)_3 \xrightarrow[-^tBuH]{+H_2O} 1/3[(^tBu)_2Al(\mu\text{-}OH)]_3 \qquad (5)$$

Thermolysis of $[(^tBu)_2Al(\mu\text{-}OH)]_3$ in an NMR sample tube indicates loss of ^tBuH and the formation of three main species that account for ca. 90% of the *tert*-butyl groups (Eq. (6)).[32]

$$[(^tBu)_2Al(\mu\text{-}OH)]_3 \xrightarrow{\Delta} [(^tBu)AlO]_6 + [(^tBu)AlO]_9 + [(^tBu)AlO]_n \qquad (6)$$

product ratio (1:2:1)

These compounds may be readily separated by fractional recrystallization and two of them have been structurally characterized by X-ray crystallography as the hexamer $[(^t\mathrm{Bu})\mathrm{AlO}]_6$ and the nonamer $[(^t\mathrm{Bu})\mathrm{AlO}]_9$.[31] The solid state structures are entirely consistent with ^{1}H, ^{13}C, ^{17}O, and ^{27}Al NMR spectroscopy and mass spectrometry. Based on mass spectrometry the third component is of higher molecular weight, i.e., $x >> 9$.

The molecular structure of $[(^t\mathrm{Bu})\mathrm{AlO}]_6$ is shown in Fig. 5, and consists of a hexagonal prism with alternating Al and O atoms. The $\mathrm{Al_3O_3}$ hexagonal faces are essentially planar with significant trigonal distortion [$\mathrm{O{-}Al{-}O_{av}}$ = 113°, $\mathrm{Al{-}O{-}Al_{av}}$ = 126°]. A similar structure has been reported for the iminoalanes, $[\mathrm{XAl(N^iPr)}]_6$ (X = H, Me, Cl).[33]

The molecular structure of the core of $[(^t\mathrm{Bu})\mathrm{AlO}]_9$ is shown in Fig. 6, and is structurally similar to $[\mathrm{Na(O^tBu)}]_9$, and is derived from two parallel six-membered $\mathrm{Al_3O_3}$ rings that are connected by three oxygen atoms and three aluminum atoms, such that every oxygen is three-coordinate and each aluminum has a coordination number of four.

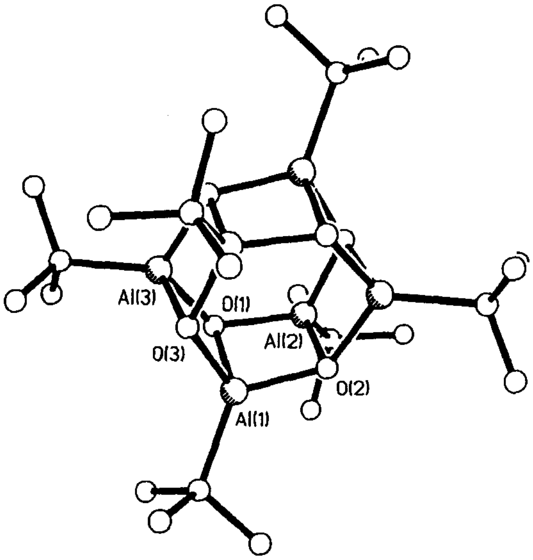


FIGURE 5 Molecular structure of $[(^t\mathrm{Bu})\mathrm{AlO}]_6$. Hydrogen atoms have been omitted for clarity.

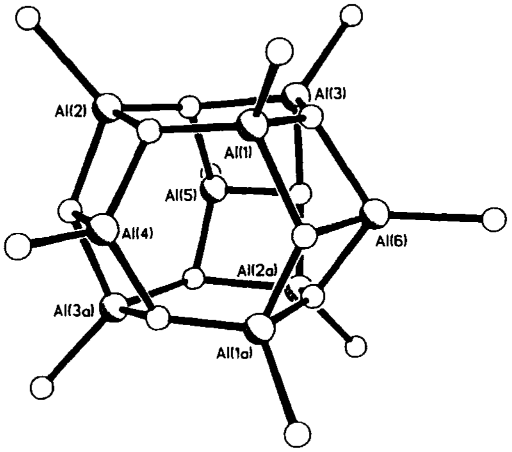


FIGURE 6 Molecular structure of [(^{t}Bu)AlO]$_9$. Methyl groups have been omitted for clarity.

While these *tert*-butyl substituted alumoxanes are at present the best models for the Kaminsky co-catalyst MAO, being entirely consistent with spectroscopic observations of the latter, further studies are clearly required to provide proof positive of their connection. However, it seems reasonable that MAO should consist of various cage compounds similar to those observed for other main group binary compounds, and not cyclic structures with coordinately unsaturated aluminum centers as traditionally proposed in the literature.

The oxygen donor chemistry of gallium is perhaps the least explored of all the group III elements. While the hydrolysis of gallium alkyls has allowed for the isolation of hydroxide complexes,[34] subsequent condensation reactions have previously yielded insoluble oligomeric materials (Eq. (7)).[34]

$$\mathrm{GaR_3} \xrightarrow[-\mathrm{RH}]{\mathrm{H_2O}} \mathrm{R_2GaOH} \xrightarrow[-\mathrm{RH}]{\Delta} \mathrm{RGaO} \qquad (7)$$

In a similar manner to the aluminum chemistry presented above, the hydrolysis of Ga(^{t}Bu)$_3$ in non-coordinating solvents yields the trimeric hydroxide, [(^{t}Bu)$_2$Ga(μ-OH)]$_3$, the gravimetric analysis date of which indicates that exothermic decomposition occurs @

140°C.[34] In contrast to the aluminum analog, however, heating $[(^tBu)_2Ga(\mu\text{-}OH)]_3$ in refluxing xylene results in the formation of only a single product, the first gallium-oxo cluster, $[(^tBu)GaO]_9$.[35] Although not characterized by X-ray crystallography, medium resolution CI mass spectrum shows peaks due to the parent ion (m/z = 1286) and the ^1H and ^{13}C NMR spectrum show the presence of two *tert*-butyl environments in a 1:2 ratio, while the ^{17}O NMR spectrum shows two oxide environments, again in a 1:2 ratio (see Fig. 7). Given the obvious analogy to $[(^tBu)AlO]_9$, i.e., replacing Al with Ga, $[(^tBu)GaO]_9$ undoubtedly has the core structure shown in **IV**. However, unlike the aluminum-oxo or gallium-sulfido (see below) clusters, no cage rearrangements or other clusters are observed for $[(^tBu)GaO]_x$.

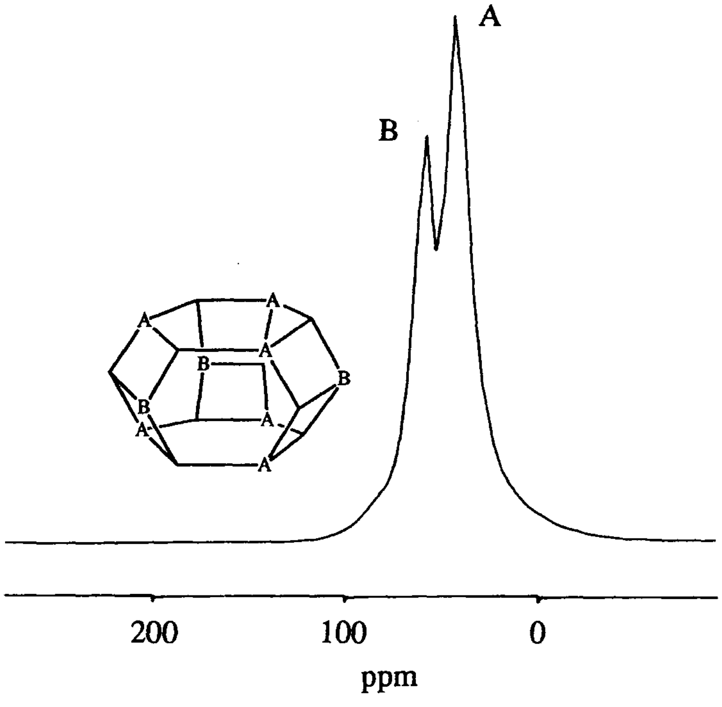
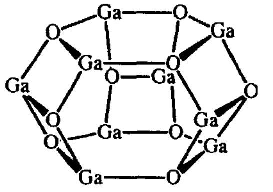


FIGURE 7 ^{17}O NMR spectrum of $[(^tBu)GaO]_9$ showing the presence of two distinct oxo environments, i.e., those within (A) and those linking (B) the two parallel hexagonal faces (see inset).



(IV)

At present there are no structural studies concerning the hydrolysis products of indium trialkyls; however, Smith, Eaborn and co-workers have reported[36] that a compound containing an adamantane like tetra-indium core was isolated as the hydrolysis product of a *tris*-trimethylsilylmethyl indium hydride (see Eq. (8)).

$$\mathrm{InCl_3} \xrightarrow[\mathrm{THF}]{\mathrm{LiC(SiMe_3)_3}} \mathrm{Li(THF)_3(\mu\text{-}Cl)InCl_2[(C(SiMe_3)_3]} \xrightarrow{\mathrm{LiAlH_4}}$$

$$\mathrm{[(Me_3Si)_3C]In(H)(\mu\text{-}H)Li(THF)_2(\mu\text{-}H)In(\mu\text{-}H)(H)}$$

$$\cdot\ \mathrm{[C(SiMe_3)_3]} \xrightarrow{\mathrm{H_2O}} \mathrm{\{[Me_3Si)_3C]In\}_4(\mu\text{-}OH)_6(\mu_4\text{-}O)} \qquad (8)$$

However, in comparison to $[L_4In_4(\mu\text{-}OH)_6]^{6+}$ (above) the indium atoms in $\{[(Me_3Si)_3C]In\}_4(\mu\text{-}OH)_6(\mu_4\text{-}O)$ are five-coordinate due to the presence of a central μ_4-oxo ligand (see Fig. 8). It is interesting that the geometry of the indium excluding the oxo-ligation is very close too tetrahedral.

While the formation of an $[In_4(OH)_4]^{8+}$ cluster was postulated for the hydrolysis of indium salts, the hydrolysis of the indium phosphinate $[Me_2In(O_2PPh_2)]_2$ in the presence of pyridine yielded the first example of an isolated group III/VI cubane cluster, $[InMe(OH)(O_2PPh_2)]_4.(py)_4$.[37] The $In_4(OH)_4$ cubane core of which is shown in Fig. 9 and consists of four six-coordinate indium atoms with four μ_3-OH groups. The pseudo-octahedral coordination sphere at each indium atom is completed by a terminally bonded methyl group and two oxygen atoms from bridging diphenyl phosphinate moieties. The four terminal methyl groups are situated two on each side of the unbridged faces.

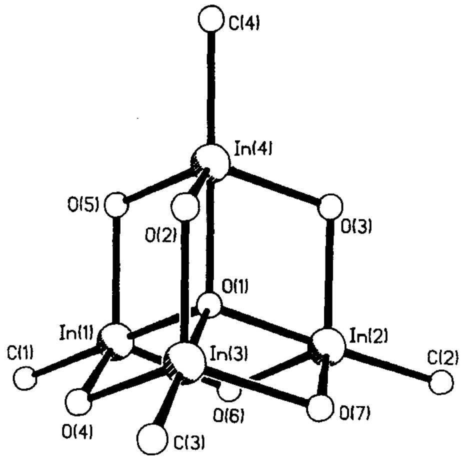


FIGURE 8 The molecular structure of $\{[(Me_3Si)_3C]In\}_4(\mu\text{-}OH)_6(\mu_4\text{-}O)$, with the Me_3Si groups omitted for clarity.

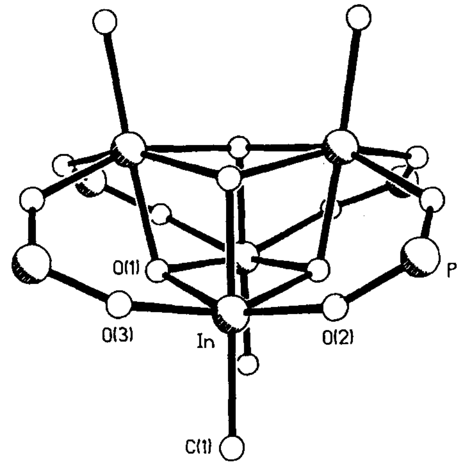


FIGURE 9 Perspective view of the core of $[InMe(OH)(O_2PPh_2)]_4(py)_4$. All hydrogen atoms, phenyl rings and pyridines have been omitted for clarity.

Although not noted at the time of publication, not only was $[InMe(OH)(O_2PPh_2)]_4.(py)_4$ the first example of a III/VI cubane compound, it was also the first six-coordinate group III alkyl to be structurally characterized.

3. SULFIDES AND SULFUR DONOR LIGANDS

While there has been no sulfur analog to the studies of the hydrolysis of group III inorganic salts, the tetra-gallium and indium anions $[M_4S_{10}]^{8-}$ (M = Ga, In) have been isolated from the reaction of M_2S_3 with aqueous metal sulfide, e.g., (Eq. (9)).

$$2\ M_2S_3 + 4\ K_2E \rightarrow K_8[M_4E_{10}] \qquad (9)$$

The structures of the potassium salts $K_8[Ga_4S_{10}].16(H_2O)$ and $K_8[In_4S_{10}].16(H_2O)$ have been determined by X-ray crystallography,[38] and contain isolated adamantane tetrameric ions $[M_4S_{10}]^{8-}$, e.g., Fig. 10, which are isostructural to the isoelectron group IV anion $[Ge_4S_{10}]^{4-}$.[39]

Similar adamantane clusters are $Ga_4I_4(SMe)_4S_2$ and $Al_4I_4(SMe)_4S_2$ prepared from the reaction of Me_2S_2 with Ga_2I_4[40] and $GaAlI_4$,[41] respectively. The molecules are isostructural with the M–S distances falling into two groups, those to the sulfide [average = 2.18 Å (Al), 2.20 Å (Ga)] and those to the methylthiolate ligands [2.30 Å (Al), 2.33 Å (Ga)]. In the case of $Al_4I_4(SMe)_4S_2$ (Fig. 11) the latter value is comparable to that observed in dimeric aluminum thiolates.[42] Although not strictly a III/VI cage compound, the

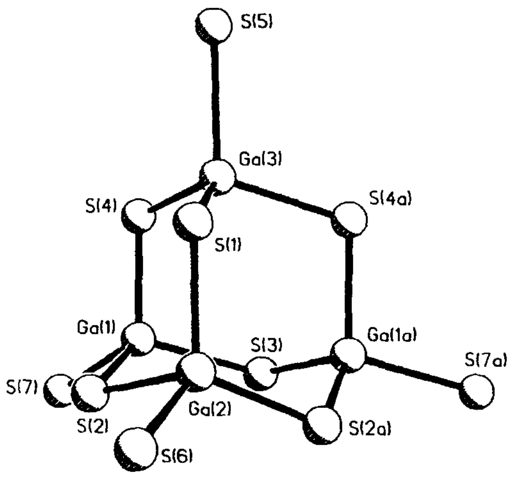


FIGURE 10 View of the $[Ga_4S_{10}]^{8-}$ anion.

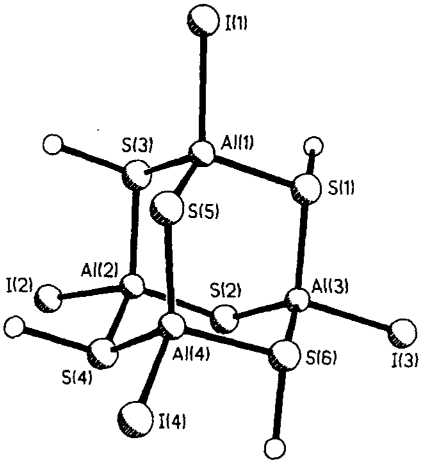
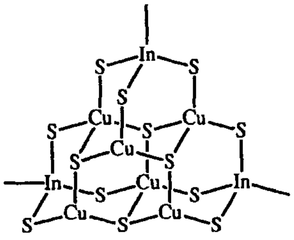


FIGURE 11 Molecular structure of $Al_4I_4(SMe)_4S_2$. Hydrogen atoms have been omitted for clarity.

copper indium thiolate cluster $[Cu_6In_3(SEt)_{10}]^-$, also contains adamantane-like core structure (V).[43]



(V)

Whereas the hydrolysis of group III alkyls allows in many cases for the isolation of intermediate hydroxide complexes (see above), which upon thermolysis at moderate temperatures results in the formation of an oxide, the reaction of MR_3 with H_2S results in the direct formation of insoluble polymeric sulfides, presumably via unstable hydrosulfido complexes.[44] However, the use of the sterically demanding *tert*-butyl group allows for the isolation of the hydrosulfido complex as well as the subsequent sulfido clusters.[45] The reaction of $Ga(^tBu)_3$ with an excess of H_2S yields the hy-

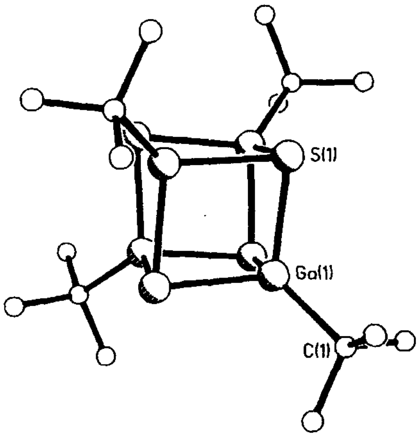


FIGURE 12 Molecular structure of $[(^t\mathrm{Bu})\mathrm{GaS}]_4$. All hydrogen atoms have been omitted and only crystallographically unique atoms are labeled for clarity.

drosulfido complex $[(^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-SH})]_2$, whose structure has been confirmed by X-ray crystallography.[45] Gentle thermolysis (either in solution or the crystalline state) of $[(^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-SH})]_2$ results in the quantitative formation of the distorted cubane cluster $[(^t\mathrm{Bu})\mathrm{GaS}]_4$ (Eq. (10)), the molecular structure of which is shown in Fig. 12.[45] The cubane cluster is also formed via the alkyl disulfide, as the only gallium containing product from the reaction of $\mathrm{Ga}(^t\mathrm{Bu})_3$ with elemental sulfur (S_8) (Eq. (11)). The aluminum sulfido cubane $[(^t\mathrm{Bu})\mathrm{AlS}]_4$ was reported to be prepared by analogous routes by Cowley, Jones *et al.*[46]; however, while characterized by NMR spectroscopy and mass spectrometry, no structural data was reported.

$$\mathrm{Ga}(^t\mathrm{Bu})_3 \xrightarrow[-^t\mathrm{BuH}]{+\mathrm{H_2S}} 1/2[(^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-SH})]_2 \xrightarrow[-^t\mathrm{BuH}]{\Delta} 1/4[(^t\mathrm{Bu})\mathrm{GaS}]_4 \qquad (10)$$

$$\mathrm{Ga}(^t\mathrm{Bu})_3 \xrightarrow{S_8} [(^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-SS}^t\mathrm{Bu})]_2 \xrightarrow{S_8} [(^t\mathrm{Bu})\mathrm{GaS}]_4 + {}^t\mathrm{Bu}(\mathrm{S})_n\mathrm{SS}^t\mathrm{Bu} \qquad (11)$$

$$n = 1, 2, 3$$

The study of iron–sulfur cage chemistry has been stimulated by the desire to understand the biochemical behavior of nonheme iron–sulfur proteins, specifically the four-iron ferrodoxins.[47] Given the analogies observed for gallium and iron aqueous chemistry[48] as a consequence of their similarity in ionic radii for six-coordinate complexes (0.620 Å for Ga^{3+} compared to 0.645 Å for Fe^{3+}),[49] it is perhaps not surprising that the gallium homologue of the Fe_4S_4 cubes prepared as synthetic representations for ferrodoxins is isolable.[50] What is notable, however, is that $[(^t\mathrm{Bu})\mathrm{GaS}]_4$ [Ga–S = 2.359(3) Å] is structurally similar not to the isoelectronic $[\mathrm{CpFeS}]_4$ [Fe–S = 2.20(8)–2.26(4) Å],[51] but to the mixed valence (formally $\mathrm{Fe^{III}Fe_3^{II}}$) trianions, $[(\mathrm{X})\mathrm{FeS}]_4^{3-}$ [Fe–S = 2.297(6)–2.351(9) Å].[52]

Although no alkyl indium sulfido cubanes have been crystallographically characterized,[53] the inorganometallic cubanes $\{[\eta^5\text{-}\mathrm{C_5H_5})\mathrm{M(CO)}_x]\mathrm{InS}\}_4$ (M = Fe, x = 2; M = Mo, x = 3), prepared from the indium halides and bis-trimethylsilylsulfide (Eq. (12)),

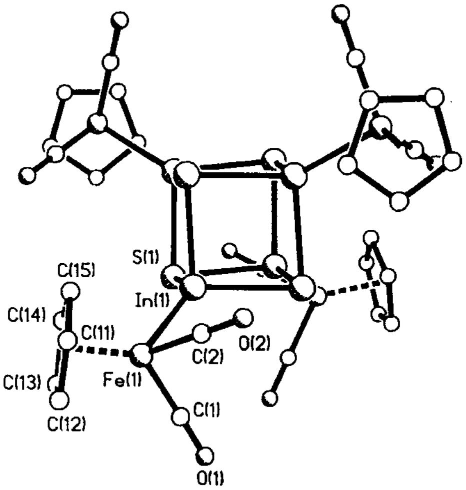


FIGURE 13 The molecular structure of $\{[\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2}]\mathrm{InS}\}_4$. For clarity all hydrogen atoms have been omitted, and only crystallographically unique atoms are labeled.

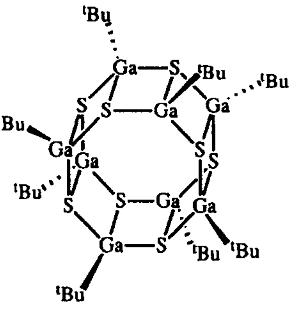
have both been structurally characterized and the iron compound is shown in Fig. 13.[54]

$$[(\eta^5\text{-}C_5H_5)M(CO)_2]InBr_2 + S(SiMe_3)_2 \rightarrow \{[(\eta^5\text{-}C_5H_5)M(CO)_x]InS\}_4 \quad (12)$$

$$M = Fe, x = 2;\ M = Mo, x = 3$$

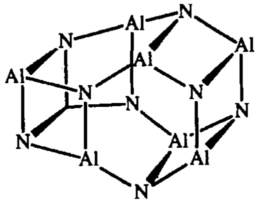
The In–S distances [2.535(1)–2.581(1) Å] are, as expected, slightly larger than in [(^{t}Bu)GaS]$_4$ analogue, but are similar for the Fe and Mo derivatives, as are the intercubane angles, i.e., In–S–In = 84.6(1)–84.9(1)° (Fe) and 84.3(2)–86.9(2)° (Mo); S–In–S = 94.9(1)–95.3(1)° (Fe), 92.7(2)–96.0(2)° (Mo). This latter observation suggests that the cubane core geometry is defined by close packing of the indium and sulfur atoms and not the steric bulk of substituents.

In the case of the gallium sulfide cubane, [(^{t}Bu)GaS]$_4$, it was observed that repeated sublimation or mild solution themolysis (refluxing pentane) resulted in the formation of an octamer [(^{t}Bu)GaS]$_8$, in low yield.[55] Mass spectral and NMR data were consistent with a drum structure (**VI**) similar to those observed for tin oxide clusters.[56]



(VI)

The presence of a single resonance for the *tert*-butyl groups in both ^{1}H and ^{13}C does preclude a structure analogous to that reported for [HAl(N^{n}Pr)]$_8$[57] and [MeAl(NMe)]$_8$,[58] i.e., (**VII**) for which two distinct sets of resonances should be observed.



(VII)

Despite the low yield in the tetramer to octamer conversion, this intriguing observation suggested that facile cluster rearrangements may occur to give higher nuclearity clusters.

Prolonged thermolysis of $[(^t\mathrm{Bu})\mathrm{GaS}]_4$ in refluxing hexane results in its near quantitative conversion to a single new species, $[(^t\mathrm{Bu})\mathrm{GaS}]_7$.[35] Like $[(^t\mathrm{Bu})\mathrm{GaS}]_4$, the heptamer is stable to oxidation and hydrolysis, both as a solid and in solution. $[(^t\mathrm{Bu})\mathrm{GaS}]_7$ sublimes intact under vacuum (240°C, 10^{-3} torr); however, it yields only $[(^t\mathrm{Bu})\mathrm{GaS}]_4$ when sublimed at atmospheric pressure.[35]

The molecular structure of $[(^t\mathrm{Bu})\mathrm{GaS}]_7$, as determined by X-ray crystallography, is shown in Fig. 14. The $\mathrm{Ga_7S_7}$, core may conceptually be considered to be deriveed from the linkage of two

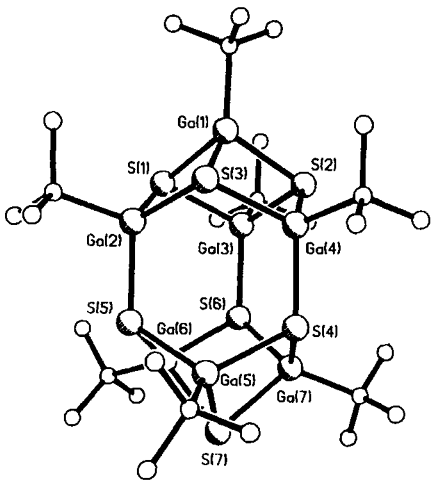
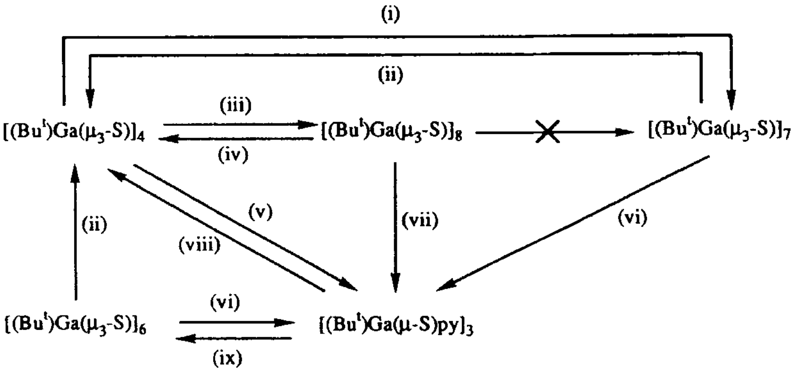


FIGURE 14 The molecular structure of $[(^t\mathrm{Bu})\mathrm{GaS}]_7$, with all hydrogen atoms omitted for clarity.

apically deficient cubanes, i.e., $({}^{t}Bu)_4Ga_4S_3$ and $({}^{t}Bu)_3Ga_3S_4$, and is similar to those reported for $[RAl(NMe)]_7$, R = Me, Et[59] and that proposed for $[EtMgO^{n}Pr]_7$.[60] The solid state structure is entirely consistent with ^1H NMR spectroscopy, three gallium coordinated *tert*-butyl environments, 1:3:3, indicating that the cage structure is retained in solution. The Ga–S bond lengths in $[({}^{t}Bu)GaS]_7$ fall into two groups: those linking, and those of the apically deficient cubane fragments [$Ga-S_{av}$ = 2.292(4) Å and 2.334(5) Å, respectively]. The latter are comparable to that observed for the cubane $[({}^{t}Bu)GaS]_4$ [2.359(3) Å], while the former is within the range observed in the adamantane-like $Ga_4I_4(SMe)_4S_2$ [2.204(8) Å][40] and $[Ga_4S_{10}]^{8-}$ [2.289(2) Å].[38] These differences are consistent with the strain inherent in the cubane derived structure.

The formation of $[({}^{t}Bu)GaS]_7$ from $[({}^{t}Bu)GaS]_4$ may suggest that the latter dimerizes to give an octamer, which subsequently decomposes to the heptamer. However, although the octamer, $[({}^{t}Bu)GaS]_8$, is formed in low yield from $[({}^{t}Bu)GaS]_4$, upon the thermolysis in pentane of the latter there is no evidence to indicate that the octamer is converted to the heptamer under more forcing conditions. Instead, NMR scale reactions are consistent with $[({}^{t}Bu)GaS]_8$ initially reforming the tetramer, which over time is subsequently converted to the heptamer.[35]

Dissolution of $[({}^{t}Bu)GaS]_n$ (n = 4, 7, 8) in pyridine results in the formation of a compound formulated, from ^1H and ^{13}C NMR,



SCHEME 1 (i) Δ, hexane, 3–4 days; (ii) sublimation, 1 atm; (iii) Δ, pentane, 12 h; (iv) Δ, pentane; (v) pyridine, mins; (vi) pyridine, 1–2 days; (vii) Δ, pyridine; (viii) vacuum sublimation; (ix) Δ, solid state.

as (^{t}Bu)Ga(S)py (see Scheme 1), which was shown by X-ray diffraction to be trimeric in the solid state, i.e., [(^{t}Bu)Ga(S)py]$_3$. The rate of dissolution/reaction of the sulfido clusters with pyridine is dependent on the cluster size; the tetramer dissolves rapidly in minutes, the hexamer (below) and the heptamer over a period of hours, while the octamer requires gentle warming.

Surprisingly the mass spectrum of an analytically pure sample of [(^{t}Bu)Ga(S)py]$_3$ did not show any of the expected peaks, but only those due to the tetramer, [(^{t}Bu)GaS]$_4$.[61] In fact, sublimation of [(^{t}Bu)Ga(S)py]$_3$ @ 230–250°C under vacuum also yields the tetramer in essentially quantitative yield (Scheme 1). By contrast, heating a sample in the solid state at 100° results in a 32% mass loss (equivalent to loss of all pyridine, calculated 33.2%) leaving a white solid, which consists of [(^{t}Bu)GaS]$_8$ and (ca. 50%) of [(^{t}Bu)GaS]$_6$, the molecular structure of which is shown in Fig. 15. The Ga_6S_6 core can be described as a hexagonal prism with alternating Ga and S atoms. The chair conformation of each Ga_3S_3 face is unlike the planar structures observed for [XAl(N^{i}Pr)]$_6$ (X = H, Me, Cl),[33] and [(^{t}Bu)AlO]$_6$ (above); however, it is closely related to that observed for the anionic clusters [$Fe_6S_6X_6$]$^-$.[62] The Ga–S distances are of two types, those within [2.316(3)–2.323(3) Å], and those linking [2.379(5)–2.392(4) Å] the two Ga_3S_3 rings.

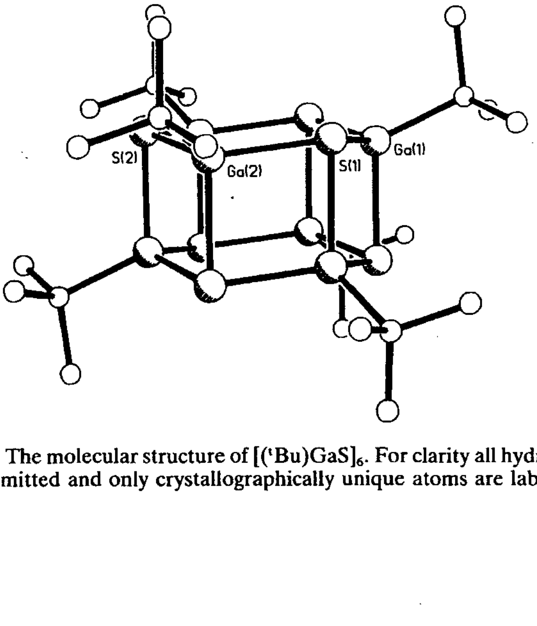


FIGURE 15 The molecular structure of [(^{t}Bu)GaS]$_6$. For clarity all hydrogen atoms have been omitted and only crystallographically unique atoms are labeled.

The topological rearrangement observed for $[(^t\text{Bu})\text{GaS}]_x$, and summarized in Scheme 1, are, if not unique in cluster chemistry (other rearrangements often being accompanied by changes in speciation), certainly the most extensive and reversible for a single well-characterized species.

4. SELENIDES AND TELLURIDES

Due to the highly toxic and odiferous nature of selenium and tellurium compounds no extensive group III cluster chemistry has been developed with selenium and/or tellurium donor ligands; however, a handful of key compounds have been reported.

The tetra-indium anion $[\text{In}_4\text{Se}_{10}]^{8-}$ has been isolated and found to be isotypic to the sulfide analogs (see above).[38] The In—Se bonds are divided into terminal [2.538(1)–2.553(1) Å] and bridging [2.552(1)–2.583(1) Å] and are all ca. 0.11 Å larger than their equivalents in the sulfido anion, consistent with the increased radius of Se^{2-} compared to S^{2-} (1.84 versus 1.70 Å). A similar difference (0.11–0.13 Å) is observed for the cubane compounds, $[(^t\text{Bu})\text{GaE}]_4$, E = S, Se.[55]

The reaction of $\text{Ga}(^t\text{Bu})_3$ with either Se_8 or H_2Se yields the cubane compound $[(^t\text{Bu})\text{GaSe}]_4$, presumably via the alkyldiselenide and hydroselenolate intermediates, respectively (Eqs. (13) and (14)).[55]

$$\text{Ga}(^t\text{Bu})_3 + \text{Se}_8 \rightarrow [(^t\text{Bu})\text{GaS}]_4 + {}^t\text{BuSeSe}^t\text{Bu} \qquad (13)$$

$$\text{Ga}(^t\text{Bu})_3 + \text{H}_2\text{Se} \xrightarrow{0°\text{C}} 1/4[(^t\text{Bu})\text{GaS}]_4 + {}^t\text{BuH} \qquad (14)$$

Alternatively the cubane compound may also be prepared by the reaction of the selenolate, $[(^t\text{Bu})_2\text{Ga}(\mu\text{-Se}^t\text{Bu})]_2$, with metallic selenium (Eq. (15)).

$$2[(^t\text{Bu})_2\text{Ga}(\mu\text{-Se}^t\text{Bu})]_2 + \text{Se}_\infty \rightarrow [(^t\text{Bu})\text{GaSe}]_4 + {}^t\text{BuSeSe}^t\text{Bu} \qquad (15)$$

The aluminum–selenide, and aluminum and gallium–telluride cubanes, have also been prepared by an analogous route to that in Eq. (15),[46] while the indium–selenide and telluride cubanes $\{[(\eta^5\text{-}C_5H_5)M(CO)_x]InE\}_4$ (M = Fe, x = 2, E = Se and M = Mo, x = 3, E = Te) have been isolated in a similar manner to the sulfides (cf. Eq. (12)).[53]

5. RELATIONSHIP OF III/VI CAGE COMPOUNDS TO SOLID STATE MATERIALS: OLD AND NEW

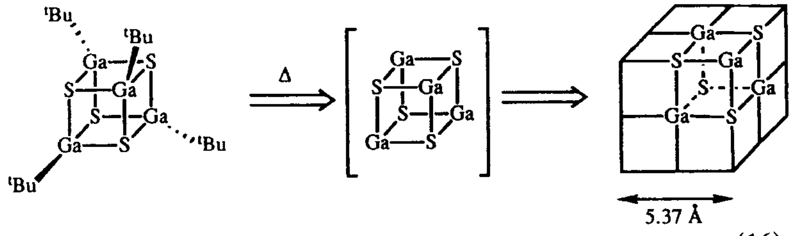
Although the number of structurally characterized group III/VI clusters is perhaps too small to be able to make detailed predictions of structure of as yet unknown compounds, the similarity of many of the structures to related solid state phases would indicate that, in the absence of significant ligand contributions, the close packing of octahedra and tetrahedra is the predominant control over the structure of III/VI clusters.

The link between cluster and solid state structures is best demonstrated by a comparison of the boehmite structure with the Al–O cores of the $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ cation and $Al_{10}(OH)_{16}(OSiEt_3)_{14}$, above. Clearly these cluster compounds can be considered as a small particle of the mineral surrounded by an organic sheath. It is also interesting that the propensity of gallium to tetrahedral rather than octahedral coordination is evident from both the instabilities of the cationic cluster $[Ga_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ and the high stability of $\beta\text{-}Ga_2O_3$ (in which half the gallium atoms are in tetrahedral sites) versus either the α- or γ-phases (where all the gallium atoms are in octahedral sites).

Less drastic, but by no means less interesting examples of this connection between the isolated clusters and their respective solid state phases are those between the adamantane chalcogenide clusters $Ga_4I_4(SMe)_4S_2$ and $[Ga_4S_{10}]^{8-}$, with the defect sphalerite structure of $\gamma\text{-}Ga_2S_3$.

Without wishing to over-extend the relationship between III/VI clusters and solid state materials, an interesting proposition arises. Can either metastable or previously unreported binary oxide or chalcogenide phases be prepared by the use of III/VI clusters with structures unrelated to thermodynamic phases? Recent work within our laboratory has taken the first step in this direction.

Perhaps the most significant advantage (and one that has only recently been appreciated) that chemical vapor deposition (CVD) has over other methods is the production of metastable materials. Most CVD processes operate far from equilibrium conditions, so that kinetically, rather than thermodynamically, favored products are produced. The use of $[(^t\mathrm{Bu})\mathrm{GaS}]_4$ as a single-source CVD precursor results in the deposition of crystalline films of chemical composition GaS, indicating that the stoichiometry of the precursor, i.e., Ga:S = 1:1, is retained in the deposited film.[63] However, from the electron diffraction pattern interplanar spacings may be calculated corresponding to a face-centered cubic (fcc) lattice with a lattice parameter $a = 5.37$ Å. The formation of this previously unreported cubic phase of GaS may readily be explained in terms of retention of the cubane precursor core in the deposited film. The distorted cubic core of the precursor [Ga–S–Ga = 82.1(1)°, S–Ga–S = 97.3(1)°] presumably "relaxes" under appropriate conditions in the deposited film, and begins to rearrange into a cubic lattice. The resulting structure would thus be expected to be a NaCl type lattice exhibiting face-centered cubic reflections, as is indeed observed (Eq. (16)).



(16)

For thin films the {200} reflection is observed indicating, a NaCl fcc structure; however, as the film becomes thicker, or upon thermal annealing, the {200} reflection becomes significantly reduced in intensity, suggesting that the structure relaxes further into a zinc blend fcc cubic structure due to a $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ shift of one of the interpenetrating fcc lattices. This previously unreported fcc cubic phase of GaS may be conceptually thought to consist of 100% gallium doped γ-$\mathrm{Ga_2S_3}$ which exists as a defect zinc blend cubic structure. The relaxation from a deposited NaCl to zinc blend structure is consistent with the predisposition of gallium for tetrahedral over octahedral coordination. It is also worth noting that the Ga–S distance in the zinc blend-film is ca. 2.4Å is comparable to those distances previously observed in isolated compounds (see above).

The formation of a cubic phase of GaS may have remained an academic curiosity except for two observations. First, not only is the lattice constant for the as-deposited cubic-GaS within 5% of that of GaAs (5.63 Å),[64] but thermal annealing (15 min @ 450°C) results in a significant expansion/relaxation, giving a measured lattice parameter of 5.5 Å. Thus, cubic-GaS is suitably lattice matched to GaAs for epitaxial growth. Second, the chemical passivation of GaAs surfaces is vital to its full utilization in semiconductor de-

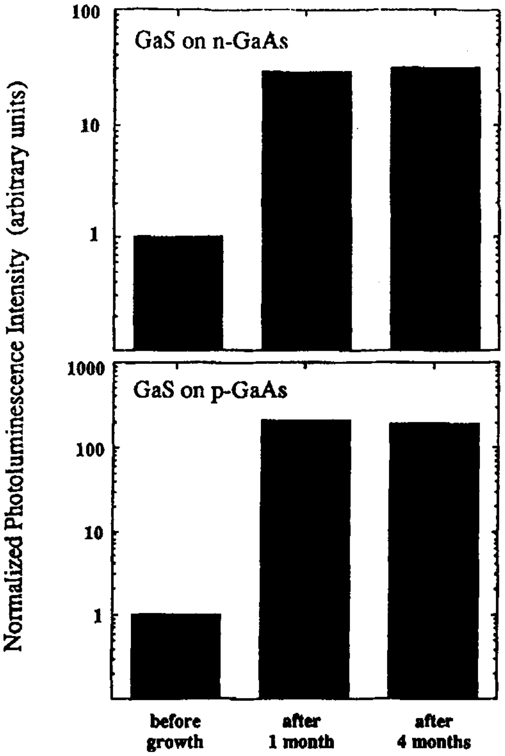


FIGURE 16 Normalized photoluminescence intensity for a typical sample of GaS vapor-deposited on GaAs. Photoluminescence intensity in arbitrary units.

vices, due to the high surface state density and the inability to form stable native oxide overlayers. Recent efforts have focused on inorganic sulfide based treatments, e.g., aqueous solutions of either Na_2S or $(NH_4)_2S$.[65] However, although the passivating effects are often comparable to the AlGaAs/GaAs benchmark, the coatings are unstable under normal laboratory conditions. Thus, it seemed to us that the cubic-GaS phase should be the perfect passivation coating for III/V semiconductors, and in particular GaAs.

Thin films of cubic-GaS were deposited onto single crystal GaAs wafers {100} by CVD, at 390°C under atmospheric pressure.[66] TEM and X-ray measurements indicate epitaxial growth of a single crystal of GaS on the GaAs substrate. The passivation of the GaS/GaAs interface was evaluated by photoluminescence intensity (PLI) measurements, since the performance of minority lifetime carrier devices is critically dependent on SRV, and experiment and theory have shown that photoluminescent response from laser irradiated semiconductors can be related to SRV. Specifically, an increase in photoluminescence may be attributed to a decrease in SRV. Figure 16 shows the dramatic increase in the PLI of both p-type and n-type GaAs samples; even more significant is that no decay in the passivation effects is noted after four months.

Not only does this result open up the possibility of technological applications for new III/VI clusters, but it suggests that new (metastable) oxide and chalcogenide phases with interesting and useful properties may be prepared from the predesigned molecular motif of a III/VI cluster compound.

Acknowledgments

I wish to thank all the graduate students, post-doctoral fellows and undergraduates who have been in my research group at Harvard over the last five years for their dedicated and skillful efforts, for their intellectual contributions, and for suffering my more bizarre ideas, in carrying out our research. I am also grateful for the support of the Aluminum Research Board and Gallia, Inc. during the writing of this review. Finally, Fred Basolo is acknowledged for asking me in the kindest possible way for a contribution!

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