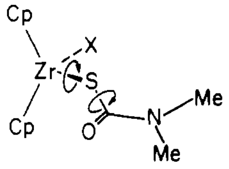
involves rotation about the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bond.

The dramatic increase in the exchange rates for the aryloxy dithiocarbamate complexes $Cp_2Zr(OPh)(Me_2dtc)$ and $Cp_2Zr(Opy)(Me_2dtc)$ is attributed to the π-donor properties of the aryloxide ligands; the rates increase as the π-donor character of the aryloxide increases in the order Opy < OPh. π-Donation from oxygen to the oxophilic Zr atom weakens the Zr–S bonds and lowers the barrier to *N*-methyl group exchange. If a $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ rotation mechanism persists in the aryloxy complexes, $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ rotation must be facilitated by preliminary rupture of a Zr–S bond (mechanism b in Figure 1) or by appreciable weakening of the zirconium-chelate interaction (mechanism c).

Alternatively, the anomalously high exchange rates for the aryloxy dithiocarbamate complexes may indicate that these complexes exchange methyl groups by a different mechanism, namely rupture of a Zr–S bond followed by rotation of the dangling ligand about the Zr–S and/or C–S bonds and subsequent reattachment of the uncoordinated S atom at the other sulfur coordination site (mechanism a in Figure 1). Zr–S bond rupture would be promoted by the π-donor properties of the aryloxide ligands, and a mechanism not involving rotation about the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bond would help to explain how methyl group exchange in the aryloxy dithiocarbamates can be appreciably *faster* than that in organic dithiocarbamates.

Finally, we ask why the π-donor properties of aryloxide ligands greatly accelerate the rate of methyl group exchange in the dithiocarbamate complexes $Cp_2ZrX(Me_2dtc)$ (X = OPh or Opy) but not in the analogous thiocarbamate $Cp_2Zr(Opy)(Me_2mtc)$. If all of the complexes rearrange by mechanism b or c, we would attribute the lack of rate acceleration in $Cp_2Zr(Opy)(Me_2mtc)$ to strong Zr-O bonding in the lateral coordination site. Since the Zr–O bond should be appreciably stronger than the corresponding Zr–S bond in the dithiocarbamates, the π-donating properties of aryloxide ligands may not be sufficient to break the Zr–O bond (mechanism b) or weaken the zirconium-chelate interaction (mechanism c).

Mechanism b or c, however, does not account for the fact that the rates of methyl group exchange in the aryloxy dithiocarbamate complexes are faster than those in organic dithiocarbamates. Therefore, we prefer a unique mechanism, mechanism a not involving rotation about the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bond, for the aryloxy dithiocarbamates. This mechanism, shown in **4**, is not accessible for aryloxy thiocarbamate complexes because rotation about the Zr–S and/or C–S bonds followed by reattachment of the uncoordinated O atom at the other coordination site, the interior site, would give the higher energy, unobserved stereoisomer that has sulfur in the lateral coordination site.[29] Consequently, even if the Zr–O bond does break in the monothiocarbamate complexes, methyl group exchange must involve rotation about the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bond.



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Conclusions. The $Cp_2ZrX(Me_2dtc)$ (X = halide or alkyl) complexes and the $Cp_2ZrX(Me_2mtc)$ (X = Cl or Opy) complexes have rates of *N*-methyl group exchange similar to those for related organic dithiocarbamates and thiocarbamates. A mechanism involving rotation about the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bond is indicated, mechanism b or c in Figure 1. The aryloxy dithiocarbamate complexes, $Cp_2ZrX(Me_2dtc)$ (X = OPh or Opy), have much higher rates of methyl group exchange, which suggests a different mechanism for these complexes, mechanism a in Figure 1 involving rupture of a Zr–S bond. This mechanism, which is promoted by the π-donor properties of the aryloxy ligands, is inaccessible in aryloxy thiocarbamate complexes because it would give a higher energy, unobserved stereoisomer.

Acknowledgment. Support for the Cornell Nuclear Magnetic Resonance Facility from the National Science Foundation Instrumentation Program (Grants CHE-79-04825 and PCM-80-18643) and the National Institutes of Health (Grant DHHS 08SORR02002A) is gratefully acknowledged. The FT-IR spectrometer was obtained with support from the National Science Foundation (Grant CHE-83-04659).

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[29] Rupture of the Zr–S bond followed by rotation of the dangling ligand and reattachment of the uncoordinated S atom at the other (lateral) coordination site would also give the unobserved stereoisomer.

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Metal Cluster Topology. 10. Polyhedral Gallium Cluster Anions in Intermetallic Phases of Gallium and Alkali Metals[1]

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Graph-theory-derived methods are used to study the chemical bonding topology in gallium-rich intermetallic phases of gallium and the alkali metals that contain globally delocalized Ga_n deltahedra ($n = 8, 11, 12$). Electron-precise chemical bonding models are presented for the following phases, assuming complete ionization of the alkali metals: (1) $MGa_3 \approx M_3(Ga_8)(Ga)$ (M = K, Rb) containing Ga_8 bisdiphenoids ("D_{2d} dodecahedra"); (2) $MGa_7 = M_2(Ga_{12})(Ga_2)$ (M = Rb, Cs) containing Ga_{12} icosahedra; (3) $K_3Ga_{13} = K_6(Ga_{11})(Ga_{12})(Ga)_3$ containing both Ga_{11} and Ga_{12} deltahedra; (4) $Na_{22}Ga_{39} = Na_{22}(Ga_{12})_2(Ga_{15})$ containing two different types of Ga_{12} icosahedra with novel Ga_{15} polyhedra in the interstices. The Ga_{15} polyhedra in $Na_{22}Ga_{39}$ have all but 1 degree 3 vertices indicative of edge-localized bonding as well as a pair of 3-coordinate gallium atoms connected by an abnormally short edge (2.43 Å) suggestive of a Ga═Ga double bond. Application of the same method to lithium/gallium phases such as Li_3Ga_{14} indicates the presence of fewer electrons than the predicted closed-shell electronic configuration in accord with the tendency of lithium atoms to form partially covalent multicenter bonds.

Introduction

The importance and stability of the deltahedral borane anions $B_nH_n^{2-}$ ($6 \leq n \leq 12$)[2,3] in boron hydride chemistry raises the question as to whether analogous species might be observed in the chemistry of the heavier congeners of boron, namely aluminum, gallium, indium, and thallium. However, so far no deltahedral metal hydride anions $M_nH_n^{2-}$ (M = Al, Ga, In, Tl) have been

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[1] For part 9 of this series, see: King, R. B. *Polyhedron* **1988**, *7*, 1813.

[2] Muetterties, E. L.; Knoth, W. H. *Polyhedral Boranes*; Marcel Dekker: New York, 1968.

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Table I. Stoichiometric Intermetallic Phases of Gallium and Alkali Metals Containing Gallium Polyhedra

intermetallic phase	gallium network[a]	deltahedra[b,c]	gallium satellite network[c,d]	ref
KGa_3, $RbGa_3$	$(Ga_8^{2-})(Ga^-)_{4/4}$	bisdisphenoid ($4Ga_8 + 4Ga$)	$Ga^-(3)$	24
$RbGa_7$, $CsGa_7$	$(Ga_{12})(Ga_2^{2-})_{6/6}$	icosahedron ($4Ga_{12} + 6(Ga_{12})_{2/3}$[e] $+ 2Ga_2$)	$Ga_2^{2-}(4)$, 2.52 Å	25
Li_3Ga_{14}	$(Ga_{12}^{2-})(Ga_2^{2-})_{6/6}$	icosahedron ($6Ga_{12} + 6Ga_2$)	$Ga_2^{2-}(3)$, 2.61 Å	26
K_3Ga_{13}	$(Ga_{12}^{2-})(Ga_{11}^{2-})(Ga)(Ga^-)_2$	icosahedron ($4Ga_{12} + 2Ga_{11} + 6Ga(11)$) edge-coalesced icosahedron ($2Ga_{12} + 4Ga_{11} + 2Ga(11) + 3Ga(4)$)	Ga(4), 3-coord $Ga^-(11)$, 4-coord	27
$Na_{22}Ga_{39}$	$(Ga_{12}^{2-})(Ga_{12}^{5-})(Ga_{15}^{15-})$	icosahedron A, Ga_{12}^{2-} ($2Ga_{12}(A) + 4Ga_{12}(B) + 6Ga_{15}$) icosahedron B, Ga_{12}^{5-} ($4Ga_{12}(A) + 2Ga_{12}(B) + 3Ga_{15} + 3LP$[f])	Ga_{15}^{15-}	28

[a] The gallium network is dissected into gallium deltahedra (Ga_8, Ga_{11}, and/or Ga_{12} depicted in Figure 1) and satellite gallium atoms. [b] The external bonding of the *n*-vertex atoms of a Ga_n deltahedron is indicated in parentheses. [c] The numbering of specific gallium atoms in parentheses corresponds to that in the original papers cited as literature references. [d] The nature of the network of satellite gallium atoms external to the Ga_8, Ga_{11}, and/or Ga_{12} deltahedra is indicated. The Ga–Ga distance is indicated for the bonded pairs of satellite gallium atoms in MGa_7 and Li_3Ga_{14}. [e] Six of the gallium vertices of the Ga_{12} icosahedra in MGa_7 are involved in *3*-center 2-electron bonds to the gallium atoms in adjacent icosahedra. [f] Three of the gallium vertices in icosahedra B of $Na_{22}Ga_{39}$ form no bonds external to the icosahedra; their external orbitals instead contain lone pairs (LP).

reported, possibly owing to the instability of metal–hydrogen bonds involving these heavier elements. However, work by Belin and Ling[4] since 1980 has shown that several of the deltahedra found in the $B_nH_n^{2-}$ borane anions,[2,3] namely those with $n = 8$, 11, and 12, are also found in gallium-rich intermetallic phases of gallium and alkali metals. Futhermore, Belin and Ling[4] demonstrate that the electron-counting methods pioneered by Wade[5,6] and Mingos[7,8] for the study of boron polyhedra as well as metal clusters can be applied to these gallium intermetallic phases.

This paper examines the polyhedral gallium cluster anions in these intermetallic phases by using the graph-theory-derived approach discussed in detail elsewhere.[9-14] These gallium clusters are not only interesting in their own right but are also potentially significant because of their relationship both to the Zintl-type anionic post-transition-metal clusters[15] and to the quasicrystalline icosahedral aluminum alloys.[16-18]

Background

The graph-theory-derived approach describes the bonding topology of metal clusters by a graph in which the vertices correspond to atoms or orbitals participating in the relevant bonding and the edges correspond to bonding relationships.[9-14] It has been shown elsewhere,[19-21] that the eigenvalues x_k of the adjacency matrix[22] of such a graph are related to the Hückel theory molecular orbital energies E_k and the Hückel parameters α, β, and S by

$$E_k = \frac{\alpha + x_k\beta}{1 + x_kS} \tag{1}$$

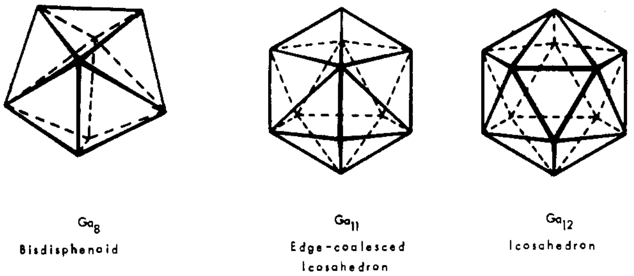

Figure 1. The three types of gallium deltahedra found in intermetallic phases of gallium and alkali metals.

Positive and negative eigenvalues are thus seen to correspond to bonding and antibonding orbitals, respectively.

In the clusters of interest in this paper, of all the vertices are gallium atoms. Such gallium vertices may be regarded as having an sp^3d^5 manifold of 9 valence orbitals, but with all 5 of the d orbitals having nonbonding electron pairs. Thus only the 4 orbitals from the sp^3 manifold participate in the metal cluster bonding as is the case for boron vertices. Among these 4 valence orbitals, 3 are normally used for intrapolyhedral skeletal bonding, leaving the fourth orbital for bonding to an external group, usually a 2-center bond to a gallium vertex of an adjacent deltahedron or to an extra "satellite" gallium atom between the gallium deltahedra. These satellite gallium atoms can be joined in pairs (e.g., in $RbGa_7$ and Li_3Ga_{14}) or even into complicated open polyhedra (e.g., a Ga_{15} polyhedron in $Na_{22}Ga_{39}$). Exceptionally, the external orbitals of the gallium vertices of the deltahedra can form 3-center Ga_3 bonds (e.g., in $RbGa_7$) or contain a nonbonding lone pair (e.g., 3 of the gallium vertices in one of the types of gallium icosahedra in $Na_{22}Ga_{39}$) like all of the vertices in the Zintl-type post-transition-metal clusters.[15,23] A gallium vertex contributing 1 electron to a 2-center external bond functions as a donor of 2 skeletal electrons like the BH vertices in the $B_nH_n^{2-}$ deltahedra. A gallium vertex with a lone pair in the external orbital functions as a donor of only a single skeletal electron consistent with the rules observed for Zintl-type post-transition-metal clusters.[10,15,23]

The two extreme types of chemical bonding in metal clusters may be called edge localized and globally delocalized.[9,11-13] An edge-localized polyhedron has 2-electron 2-center bonds along each edge of the polyhedron and is favored when the numbers of internal orbitals of the vertex atoms match the vertex degrees (the number of edges meeting at a vertex is its degree). A globally delocalized polyhedron has a multicenter core bond in the center of the polyhedron and is favored when the numbers of internal orbitals do *not* match the vertex degrees. Fully globally delocalized polyhedra are *deltahedra* without degree 3 vertices, where a deltahedron is defined as a polyhedron in which all faces are triangles. The deltahedra of interest in polyhedral gallium cluster anion chemistry (Figure 1) are the 8-vertex bisdisphenoid ("D_{2d}

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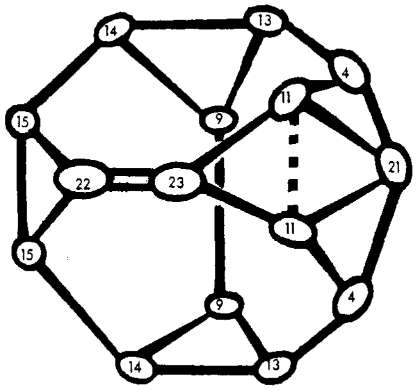

Figure 2. Ga_{15} satellite polyhedron found in $Na_{22}Ga_{39}$. The relatively long 2.99-Å Ga(11)- - -Ga(11) edge is indicated by a dotted rather than a solid line. The relatively short 2.43 Å Ga(22)=Ga(23) edge postulated to be a gallium–gallium double bond is indicated by a double line.

dodecahedron") found in $RbGa_3$, the 11-vertex edge coalesced icosahedron ("octadecahedron") found in K_3Ga_{13}, and the 12-vertex icosahedron found in several of the gallium derivatives. In the globally delocalized deltahedra the 3 internal orbitals of the vertex atoms are partitioned into 2 twin internal orbitals and a single unique internal orbital. The twin internal orbitals overlap pairwise in the surface of the deltahedron and the unique internal orbitals overlap completely to form a multicenter core bond at the center of the deltahedron.[9,11-13] The globally delocalized deltahedra with n vertices thus have $2n + 2$ skeletal electrons with $2n$ of these electrons arising from the surface bonding and the remaining 2 electrons occupying the single bonding molecular orbital arising from the multicenter core bond.[9,11-14]

The structures of the intermetallic phases of gallium and alkali metals of interest in this paper (Table I) consist of infinite networks of linked gallium polyhedra with alkali metals in some of the interstices. The alkali metals are assumed to form monopositive ions, thereby donating one electron to the gallium network for each alkali-metal atom. This pure ionic model breaks down somewhat for the lithium/gallium phases, which may have fewer electrons than the predicted closed-shell configurations, as was recognized by Belin and Ling[4] for Li_3Ga_{14}. This may be attributed to the tendency for lithium to form partially covalent $LiGa_n$ multicenter bonds so that the valence electron from a single lithium atom is effectively shared with more than one gallium atom.

A three-dimensional structure consisting of linked gallium deltahedra and alkali-metal atoms still has holes in it that can be filled by additional gallium atoms which are *not* vertices of the deltahedra. Such "satellite" gallium atoms typically form four 2-electron 2-center bonds and thus bear a formal negative charge. Satellite gallium atoms can be bonded to other satellite gallium atoms as well as to gallium atoms that are vertices of deltahedra. In $Na_{22}Ga_{39}$ the 15-vertex polyhedron formed by the satellite gallium atoms (Figure 2), which has mainly degree 3 vertices, may be regarded as an edge-localized polyhedron in contrast to the globally delocalized deltahedra.

Polyhedral Gallium Clusters

Table I lists the five structural types of stoichiometric intermetallic phases of gallium and alkali metals containing gallium polyhedra. For each structural type the following is indicated: (a) the dissection of the infinite gallium network into the individual Ga_n (n = 8, 11, 12) deltahedra (Figure 1) and groups of satellite gallium atoms; (b) the external bonds from each of the vertex atoms of each gallium deltahedron; (c) the nature of the network of the satellite gallium atoms, i.e. those not contained in any of the gallium deltahedra. Specific features of the individual structural types are outlined below.

(A) KGa_3, $RbGa_3$. These phases[24] may be represented as $M_3(Ga_8)(Ga)$ in which the Ga_8 deltahedron is a bisdisphenoid (Figure 1) with 4 degree 4 vertices (Ga(2) in ref 24) and 4 degree 5 vertices (Ga(1) in ref 24). The degree 5 gallium vertices are linked to the degree 5 gallium vertices of adjacent bisdisphenoids (Ga–Ga = 2.61–2.74 Å) whereas the degree 4 vertices are linked to the degree 4 vertices of adjacent bisdisphenoids through the 4-coordinate satellite gallium atoms (Ga(3) in ref 24). The closed-shell electronic configurations of Ga_8^{2-} for the bisdisphenoids with 2-center external bonds from each vertex atom and Ga^- for the 4-coordinate satellite gallium atoms lead to the observed stoichiometry $M_3(Ga_8)(Ga) = MGa_3$.

(B) $RbGa_7$, $CsGa_7$. These phases[25] may be represented as $M_2(Ga_{12})(Ga_2)$ with a Ga_{12} icosahedron and a bonded pair (Ga–Ga = 2.52 Å) of 4-coordinate satellite gallium atoms (Ga(4) in ref 25). Six of the gallium vertices of each Ga_{12} icosahedron are bonded externally to other gallium atoms through 2-center 2-electron bonds whereas the other 6 gallium vertices are bonded externally to other gallium atoms through 3-center 2-electron bonds. In such a situation the $2n + 2 = 26$ skeletal electron closed-shell electronic configuration of a gallium icosahedron is not the usual Ga_{12}^{2-} ion but neutral Ga_{12} determined as follows:

valence electrons of 12 Ga atoms: (12)(3)	36 electrons
required for 6/2 external 2-center 2-electron bonds: (6/2)(2)	−6 electrons
required for 6/3 external 3-center 2-electron bonds: (6/3)(2)	−4 electrons
net electrons remaining for skeletal electrons	26 electrons

The closed-shell electronic configurations of Ga_{12} for the gallium icosahedra and Ga_2^{2-} for the bonded pairs of 4-coordinate satellite atoms lead to the observed stoichiometry $M_2(Ga_{12})(Ga_2) = MGa_7$.

(C) Li_3Ga_{14}. This phase[26] may be represented as $Li_3(Ga_{12})(Ga_2)$ with a Ga_{12} icosahedron and a bonded pair (Ga–Ga = 2.61 Å) of 4-coordinate satellite gallium atoms (Ga(3) in ref 26). In each gallium icosahedron 6 of the vertices are linked directly to vertices of adjacent gallium icosahedra and the other 6 vertices are linked to the satellite gallium atoms in all cases by 2-center 2-electron bonds leading to the Ga_{12}^{2-} closed-shell electronic configuration. The overall Li_3Ga_{14} stoichiometry is 1 electron short per formula unit of the closed-shell electronic configuration $(Ga_{12}^{2-})(Ga_2^{2-}) = Ga_{14}^{4-}$, assuming complete ionization of the lithium to Li^+. However, as noted above, multicenter $LiGa_n$ bonding may relieve such apparent electron deficiencies.

(D) K_3Ga_{13}. This phase[27] may be represented as $K_6(Ga_{11})(Ga_{12})(Ga)_3$ with equal quantities of Ga_{11} and Ga_{12} deltahedra (Figure 1) and 3 satellite gallium atoms for each 23 (i.e., $Ga_{11} + Ga_{12}$) deltahedral gallium atoms. Each vertex atom in both types of gallium deltahedra forms one 2-center 2-electron external bond leading to the closed shell electronic configurations Ga_{11}^{2-} and Ga_{12}^{2-}. There are both 3-coordinate (Ga(4) in ref 27) and 4-coordinate (Ga(11) in ref 27) satellite gallium atoms with twice as many 4-coordinate gallium atoms as 3-coordinate satellite gallium atoms. The electronic configurations of Ga_{11}^{2-} and Ga_{12}^{2-} for the gallium deltahedra, Ga^- for the 4-coordinate satellite gallium atoms, and Ga for the 3-coordinate satellite gallium atoms lead to the observed stoichiometry $K_6(Ga_{11})(Ga_{12})(Ga^{3\text{-coord}})(Ga^{4\text{-coord}})_2 = K_6Ga_{26} = K_3Ga_{13}$.

(E) $Na_{22}Ga_{39}$. This phase[28] may be represented as $Na_{22}(Ga_{12})_2(Ga_{15})$ with two different types of Ga_{12} icosahedra in equal quantities and open Ga_{15} polyhedra of satellite gallium atoms with the topology depicted in Figure 2 labeling the gallium atoms as in ref 28. Except for the relatively long Ga(11)–Ga(11) edge (2.99 Å)[28] depicted as a dotted line in Figure 2, which may not represent a gallium–gallium bond, the Ga_{15} polyhedron of satellite gallium atoms has all vertices except Ga(21) of degree 3, suggestive of edge-localized bonding using 3 of the 4 valence orbitals of the sp^3 manifolds from each gallium vertex. In addition, each of the gallium vertices of the Ga_{15} satellite polyhedron except for Ga(22) and Ga(23)[28] is bonded through 2-center 2-electron bonds to

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exactly 1 gallium vertex of another polyhedron. The Ga(22)–Ga(23) distance of 2.43 Å is 0.1 Å shorter than the next shortest Ga–Ga distance (Ga(4)–Ga(13) = 2.53 Å), which when coupled with the lack of exopolyhedral bonds from Ga(22) and Ga(23) suggests a Ga(22)═Ga(23) double bond. If this is the case, the closed-shell electronic configuration for the edge-localized gallium satellite polyhedron depicted in Figure 2 in Ga_{15}^{15-}.

Now consider the two types of Ga_{12} icosahedra in $Na_{22}Ga_{39}$. In one type of Ga_{12} icosahedron (icosahedra A in ref 28) all 12 vertices form 2-center 2-electron external bonds (Table I) to gallium vertices either of other icosahedra or of the satellite Ga_{15} polyhedron leading to the usual closed-shell electronic configuration Ga_{12}^{2-}. However, in the other type of Ga_{12} icosahedron in $Na_{22}Ga_{39}$ (icosahedra B in ref 28), 3 of the 12 vertices are not bonded to external groups, leading to the 26 skeletal electron Ga_{12}^{5-} closed-shell electronic configuration as follows:

valence electrons of 12 Ga atoms (12)(3)	36 electrons
−5 charge on Ga_{12}^{5-}	+5 electrons
required for 9/2 external 2-center 2-electron bonds: (9/2)(2)	−9 electrons
required for 3 external lone pairs: (3)(2)	−6 electrons
net electrons remaining for skeletal electrons	26 electrons

The closed-shell electronic configurations of Ga_{12}^{2-} for icosahedra A, Ga_{12}^{5-} for icosahedra B, and Ga_{15}^{15-} for the edge-localized gallium satellite polyhedron (Figure 2) lead to the observed stoichiometry $Na_{22}(Ga_{12})_2(Ga_{15})$ = $Na_{22}Ga_{39}$.

Summary

This paper shows how the gallium deltahedra found in the intermetallic phases of gallium and alkali metals have geometries and chemical bonding topologies similar to those found in the deltahedral borane anions $B_nH_n^{2-}$ ($6 \leq n \leq 12$). This suggests the possibility of preparing globally delocalized deltahedral gallane anions $Ga_nH_n^{2-}$ ($6 \leq n \leq 12$) if appropriate methods can be found for forming the gallium deltahedra without breaking all of the normally very labile Ga–H bonds. In addition, the observation of an apparent Ga═Ga double bond in the Ga_{15} satellite polyhedron of $Na_{22}Ga_{39}$ suggests the possibility of preparing molecular species, such as the dianions $[R_2Ga{=}GaR_2]^{2-}$ (R = bulky alkyl groups), containing Ga═Ga double bonds. Finally the occurrence of M_{12} (M = B, Ga) icosahedra in both boron and gallium compounds (e.g., $B_{12}H_{12}$ and $RbGa_7$) as well as the existence of many aluminum alloy icosahedral quasicrystalline phases[16–18] suggests a unique tendency of the elements in the B, Al, Ga, In, Tl column of the periodic table to form icosahedral clusters exhibiting 5-fold symmetry. This feature could be used to call the elements of this column of the periodic table the "icosogens" similar to the pnicogens (N, P, As, Sb, Bi), chalcogens (O, S, Se, Te, Po), halogens (F, Cl, Br, I, At), etc.

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Registry No. Ga, 7440-55-3; KGa_3, 51681-98-2; $RbGa_3$, 79882-69-2; $RbGa_7$, 80261-97-8; $CsGa_7$, 86377-00-6; Li_3Ga_{14}, 82794-14-7; K_3Ga_{13}, 74486-98-9; $Na_{22}Ga_{39}$, 81741-48-2.

Contribution from the Naval Research Laboratory,
Code 6120, Washington, D.C. 20375

Chemical Vapor Deposition Experiments Using New Fluorinated Acetylacetonates of Calcium, Strontium, and Barium

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The calcium, barium, and strontium complexes of trifluoroacetylacetone (H[TFA]) and hexafluoroacetylacetone (H[HFA]) have been prepared and characterized by IR and ^1H and ^{19}F NMR spectroscopies, melting and sublimation points, elemental analysis, and mass spectroscopy. Chemical vapor deposition experiments were performed with all the HFA complexes and with $Ca[TFA]_2$. Under an oxygen atmosphere, metal fluoride films were deposited onto silicon substrates, but in the absence of oxygen, the films had a high carbon content. Films were characterized by Auger electron spectroscopy, X-ray diffraction, thickness measurements, and scanning electron microscopy.

Introduction

There has been considerable interest in recent years in the development of new precursors for the chemical vapor deposition (CVD) of inorganic materials. In general, such precursors must be volatile, have sufficient stability to transport to the deposition site, and decompose cleanly to give the desired material. Various acetylacetonate complexes of both main-group and transition metals have been used to deposit films of metals,[2] metal oxides,[3–9] and fluorides.[10] Complexes of fluorinated acetylacetone ligands such as $F_3CC(O)CH_2C(O)CH_3$ (H[TFA]) and $[F_3CC(O)]_2CH_2$ (H[HFA]) often have greater volatility than their hydrogen analogues. The complexes $Ca[TFA]_2$ and $Ba[TFA]_2$ have been reported previously,[11] and $Ba[HFA]_2$ is commercially available[12] (although no details of its synthesis have been published). A recent report[3] describes the use of $Ba[HFA]_2$ to prepare films of Y-Ba-Cu-O. The deposition of BaF_2 from $Ba[HFA]_2$ is also mentioned, but no details are given. Here we report the results of film growth experiments with the HFA and TFA complexes

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