Appendix

The calculations have been carried out by using the extended Hückel method with the weighted H_{ij} formula.[25] The idealized octahedral structure of **1** assumed Os–C, C–O, and Os–H distances of 1.92, 1.14, and 1.65 Å, respectively.[26] The geometry of **5** was adapted from ref 18 and has Ir–Cp(center), Ir–P, and Ir–H distances of 1.85, 2.24, and 1.70 Å, respectively, with Cp(center)–Ir–P and P–Ir–H angles of 120° and cis H–Ir–H angles of 60° with all three hydrides lying in a plane perpendicular to the Cp(center)–Ir–P plane. All the organic molecules and ligands have standard bond lengths and angles.[27] The parameters for Os and Ir are given in Table IV.

Note Added in Proof. In order to verify that the difference in C–H and M–H distances were not influencing the difference between organic and inorganic hydrides we have carried out calculations on SiH_4 and SiH_5^+ (Si–H = 1.40 Å). The results are very similar to the CH_4 and CH_5^+ cases, respectively.

---

(25) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

(26) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

(27) Pople, J. A.; Beveridge, D. L. *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970; p 111.

Fused and Linked Deltahedral Clusters in the Chemistry of the Group 13 Elements

Jeremy K. Burdett*,[†] **and Enric Canadell***,[‡]

Contribution from the Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637, and Laboratoire de Chimie Théorique, Université de Paris Sud, 91405 Orsay, France. *Received January 31, 1990*

Abstract: The electronic requirements associated with the linking and fusion via vertex, edge, and face of main group deltahedra are examined by using molecular orbital and tight-binding ideas. The focus is on the chemistry of borides and gallides. For the vertex-linked case it is shown how the traditional ideas of a mixture of multicentered intradeltahedral bonding and localized interdeltahedral bonding naturally fall out of an energy band model. The electron-counting rules for fusion turn out to be considerably more complex than those previously developed for their transition-metal analogues. Especially the interactions between orbitals on atoms not formally included in the fusion process need to be considered. As a result the electron-counting rules are often dependent upon the identity of the deltahedron itself and whether is of the closo, nido, or arachno type. The rules are used to organize the structures of a number of solid-state borides and gallides. A new rule is discovered concerning the electron count per group 13 atom found in extended solid-state structures. It appears that no deltahedral units are found in solids where the number of electrons per deltahedral boron or gallium atom exceeds 3.5. In all materials where the electron count is higher, structures containing six-membered rings or other open structures are found. The result is very different from that found in molecular boranes, where no such restriction occurs. The difference is attributed to the greater structural versatility of the solid-state. Some of the electronic reasons behind the difference between boron and gallium structural chemistry are explored.

Introduction

Chemists have had a long-standing interest in the structures and reactivity of atomic clusters, both as in small molecules and as the building blocks of infinite solids.[1,2] The discovery of the correct way to count electrons[3] and the development of the isolobal analogy[4] provided dramatic advances in our understanding of these systems and provoked several studies[5-8] of why such schemes work. Today we have sets of rules which are capable of giving the electron counts favored for polyhedra and especially deltahedra of various types.[9] Much of the attention in this field has centered around transition-metal-based polyhedral molecules, and the recent topological electron-counting schemes of Mingos[5b,c] and Teo[7] are largely concerned with molecules containing elements from this part of the periodic table. We will see, however, that these rules do not work in general when applied to fused boron or gallium deltahedra, the topic of this paper.

In extended solid-state arrays the clusters will be joined together to build up the structure. **1–4** show some one-dimensional examples of the different ways in which the solid may be assembled. **1** contains *linked* polyhedra but in **2–4** the polyhedra are *fused* together. In the latter, although the octahedron is clearly visible, the repeating unit of the structure is a smaller fragment: B_3, B_4, and B_5 for face, edge and vertex sharing, respectively. In two and three dimensions these building blocks may be linked or fused in turn to give an enormous variety of structures. The majority of the known examples contain frameworks made up of main-group atoms. That of CaB_6[10] contains B_6 vertex-linked octahedra (**5**) and that of KGa_3,[11] Ga_8 dodecahedra (**6**) linked via gallium atom

---

[†] Permanent address: Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, IL 60637.

[‡] Permanent address: Laboratoire de Chimie Théorique, Université de Paris Sud, 91405 Orsay, France.

(1) Simon, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1.

(2) Wells, A. F. *Structural Inorganic Chemistry*; Clarendon Press: Oxford, 1984.

(3) (a) Wade, K. *Chem. Commun.* **1971**, 792. (b) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *21*, 711.

(4) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

(5) (a) Mingos, D. M. P. *Nature (Phys. Sci.)* **1972**, *236*, 99. (b) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311. (c) Mingos, D. M. P.; Johnston, R. L. *Struct. Bonding* **1987**, *68*, 31.

(6) (a) Stone, A. J. *Mol. Phys.* **1980**, *41*, 1339. (b) Stone, A. J. *Inorg. Chem.* **1982**, *21*, 2297. (c) Stone, A. J.; Wales, D. J. *Mol. Phys.* **1987**, *61*, 747.

(7) (a) Teo, B. K. *Inorg. Chem.* **1984**, *23*, 1251, 1257. (b) Teo, B. K. *Inorg. Chem.* **1985**, *24*, 4209.

(8) Burdett, J. K. *Molecular Shapes*; Wiley: New York, 1980.

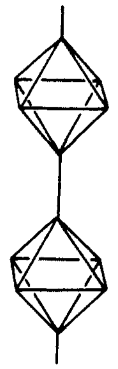
(9) The rules are not completely successful. See, for example: (a) Cave, R. J.; Davidson, E. R.; Sautet, P.; Canadell, E.; Eisenstein, O. *J. Am. Chem. Soc.* **1989**, *111*, 8105. (b) Whitmire, K. H.; Ryan, R. R.; Wasserman, H. J.; Albright, T. A.; Kang, S.-K. *J. Am. Chem. Soc.* **1986**, *108*, 6831.

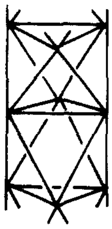
(10) See ref 2, p 1056.

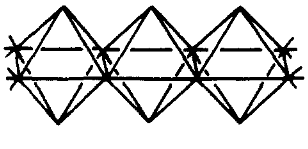
(11) Belin, C.; Ling, R. G. *C. R. Acad. Sci. Ser. B* **1982**, *294*, 1083.

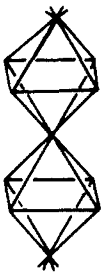
0002-7863/90/1512-7207$02.50/0

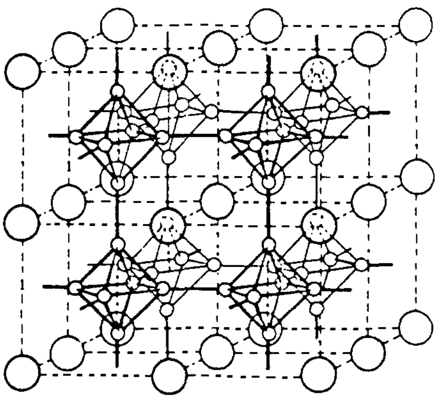
spacers. MgB_4[12] contains chains of edge-fused nido pentagonal bipyramids (**7**) in turn vertex-linked to each other.


1


2

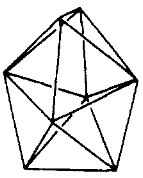

3

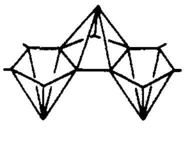

4

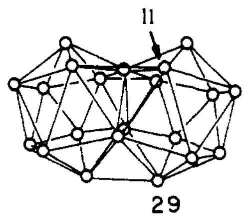

5

Some of the materials adopt structures of considerable complexity, especially those examined by Belin and co-workers. In $Rb_{0.6}Na_{6.25}Ga_{20.02}$[13] there are face-fused icosahedral dimers, **8**, of stoichiometry Ga_{21} which are vertex-linked to other such units as well as to single Ga_{12} icosahedra. Such a fragment is also found in the structure of tetragonal (or β) boron. In $Rb_{0.6}Na_{6.25}Ga_{20.02}$ and in other structures, such as that of AlB_{12}, which contain such units, not all of the sites have an occupancy of 100%. This means that these fused polyhedra are of the nido, arachno, or even hypho types. Triply fused icosahedra are also known, examples being found in $K_4Na_{13}Ga_{49.57}$[14] and in the β-rhombohedral structure of boron. We shall reserve treatment of these systems for elsewhere.

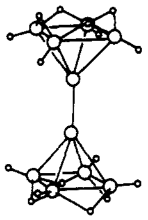
In this paper we are interested in examining the electron-counting rules for joining main-group deltahedra together, with special attention to the geometrical and electronic restrictions of the solid state. As we have pointed out above, the extension of the existing counting rules to such systems containing main-group atoms is not straightforward. Belin et al.[13-15] and Schäfer[16] have studied such systems by using Wade's rules and have estimated the number of electrons needed. We will show below that the counting rules for deltahedral fusion or linkage often depend upon the size of the polyhedron itself, results at variance with those for clusters based on transition metals. We will also be interested in exploring the reasons behind the very different structural chemistry found for molecules and solids containing these elements. Thus, while nido octahedra are common in the molecular chemistry of the boranes, no examples of vertex-linked nido octahedra, pentagonal bipyramids, or dodecahedra, for example, are found in solids.


6


7



8


9

Vertex-Linked Deltahedra. We begin by examining the electronic structure of materials containing deltahedra which are linked either to other deltahedra directly or via isolated atoms, dimers, or trimers. Examples of each type include CaB_6[10] (**5**), KGa_3,[11] YB_4,[17] and "B_4C" ($B_{13}C_2$),[18] respectively. The rules for electron counting here are just those derived for molecular clusters. We may regard each exo deltahedral bond as a two-center two-electron one but consider the bonding within each cluster as multicentered. **9** shows the structure of one isomer of $B_{10}H_{16}$, really two B_5H_9 units joined by removal of H_2. The solid-state examples of CaB_6 and $B_{13}C_2$ are classic ones treated in this way by Longuet-Higgins and Roberts in the fifties.[19,20] Of interest, however, is how the band structure of the polymeric units may be built up from the orbitals of the deltahedral parent. For those systems without any units separating the polyhedra to be joined, there are strong geometrical restrictions on the generation of three-dimensional solids. Clearly as in CaB_6 (**5**) the octahedron is a legitimate unit, but it is not possible for example to link icosahedra or tricapped trigonal prisms together to produce a three-dimensional solid solely by single atomic contacts between them. One-dimensional chains are possible for any deltahedron. The MB_{12} structure consisting of linked cuboctahedra[21] is the only other known structure constructed by using the building algorithm shown in **5** for CaB_6. We shall see via the energy band structure of the crystalline solid how the counting rules result for structures of this type. We note that Longuet-Higgins and Roberts performed a (rather simple) tight-binding calculation on CaB_6 many years ago.[19]

Let us first consider the one-dimensional system built from vertex-linked octahedra B_6H_4 (**1**). It can be considered as a fragment of the CaB_6 structure where the missing links have been "saturated" with hydrogens. The band structure is reported in Figure 1 along with the energy levels of the "unit cell" B_6H_4. The lowest band ($1a_1$)/energy level ($1a_1$) of these systems is not shown in Figure 1. There is a band gap of 3.9 eV for an occupation of 12 bands, which corresponds to $B_6H_4^{2-}$. This is exactly the same electron count corresponding to the isolated octahedral cluster (i.e., $B_6H_6^{2-}$). In other words, the fact that the cluster has been

---

(12) Naslain, R.; Guette, A.; Barret, M. *J. Solid State Chem.* **1973**, *8*, 68.

(13) Charbonnel, M.; Belin, C. *J. Solid State Chem.* **1987**, *67*, 210.

(14) Belin, C.; Charbonnel, M. *J. Solid State Chem.* **1986**, *64*, 57.

(15) Belin, C.; Ling, R. G. *J. Solid State Chem.* **1983**, *48*, 40.

(16) Schäfer, H. *J. Solid State Chem.* **1985**, *57*, 97.

(17) Zalkin, A.; Templeton, D. H. *Acta Crystallogr.* **1953**, *6*, 269.

(18) See ref 2, p 1050.

(19) Longuet-Higgins, H. C.; Roberts, M. de V. *Proc. Roy. Soc.* (*London*) **1954**, *A224*, 336.

(20) Longuet-Higgins, H. C.; Roberts, M. de V. *Proc. Roy. Soc.* (*London*) **1955**, *A225*, 110.

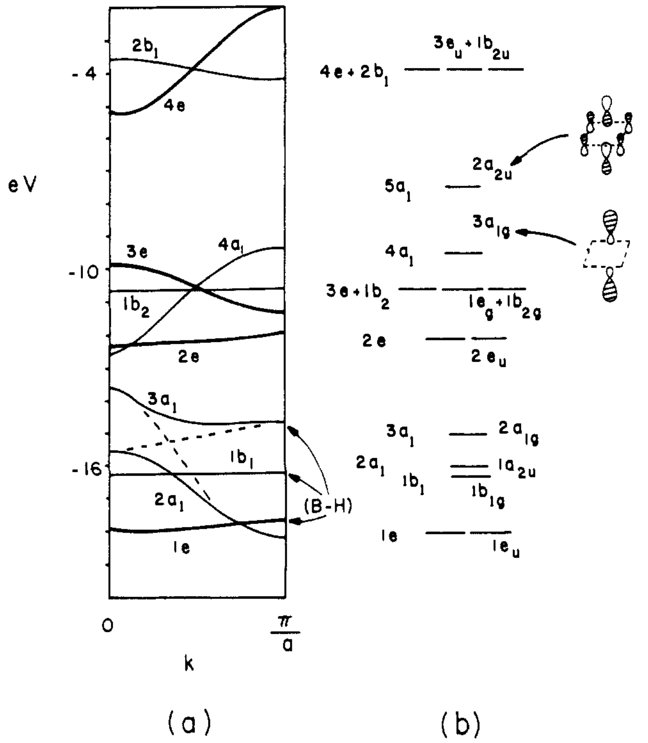
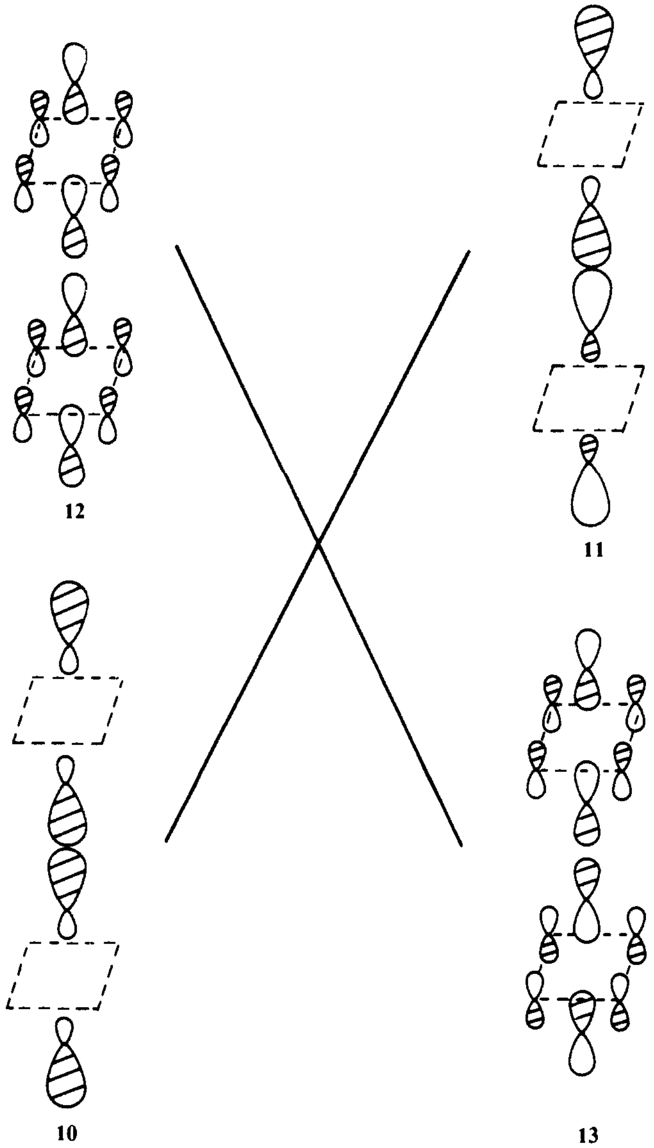


Figure 1. Band structure for a B_6H_4 chain (a) and energy levels for a B_6H_4 unit (b). The lowest band ($1a_1$) in (a) and energy level ($1a_1$) in (b) have been omitted. Thick and thin lines in the band structure represent doubly degenerate and nondegenerate bands, respectively.



embedded in an infinite structures does not change the relationship between stability and electron count.

How this comes about is easy to see by looking in some detail at the results of Figure 1. The levels there have been labeled according to the C_{4v} symmetry group which is the appropriate one for the one-dimensional system. Labeling in D_{4h} is also included for the discrete unit B_6H_4. Except for the $3a_{1g}$ and $2a_{2u}$ levels, all the unit cell levels can be easily related to the different bands of the chain. Some of them, like $3e_u$ or $1e_g$, acquire a non-negligible dispersion (2–4 eV). $3a_{1g}$ and $2a_{2g}$, i.e., the two lone pair orbitals of the B_6H_4 unit, are both of a_1 symmetry in the C_{4v} group. Repetition in-phase ($k = 0$) or out-of-phase ($k = \pi/a$) of the $3a_{1g}$ orbital gives crystalline orbitals (**10** and **11**) which are essentially bonding and antibonding across the links. As shown in **12** and **13**, just the opposite is found in the case of the $2a_{2u}$ unit cell orbital. Since both orbitals are strongly concentrated in the vertex-linked sites, the intended crossing is strongly avoided, and only one of the bands ($4a_1$) stays within the bunch of bonding and nonbonding levels. The fact that this band shows some dispersion is due to the change in the nature of the intraunit cell interactions along the chain direction which are nonbonding at $k = 0$ (**10**) but antibonding at $k = \pi/a$ (**13**). In consequence, this band describes the series of slightly interacting two-center two-electron interoctahedral bonds.

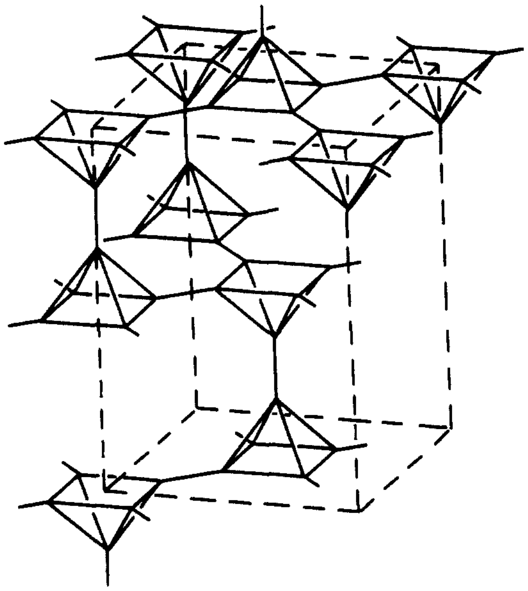
Although in this particular case the top of the $4a_1$ band lies at almost the same energy as the top of the 3e one, the crucial fact leading to the existence of a band gap is that the π-type interactions along the chain, which are responsible for the dispersion of the frontier e bands, are not strong enough to close the gap between the two groups of orbitals descending from the t_{2g} and t_{2u} frontier orbitals of the octahedron (i.e., the $1e_g$ and $3e_u$ levels of the B_6H_4 fragment). The main reason for this is that the two pairs of frontier e levels describe respectively bonding/antibonding interactions along one of the squares of the octahedra (i.e., implicate four B–B contacts per unit cell), whereas the inter-unit cell π-interactions implicate only one B–B contact per unit cell. The effect of the last interaction is thus small relative to the first one which determines the initial separation. In conclusion, the bonding in the B_6H_4 chain can be described as a combination of classical two-center two-electron interoctahedral localized bonding and nonclassical intraoctahedral delocalized electron-deficient bonding.

The same analysis can be applied to any vertex-linking (one-, two-, or three-dimensional) of main-group deltahedra (closo, nido). It also applies to other nondeltahedral polyhedra which can generate infinite systems by using this building algorithm, as is the case for the three-dimensional framework of vertex-linked cuboctahedra of the MB_{12} structure. In all these cases, the appropriate electron count for high stability can be found by simply adding as many electron pairs as interpolyhedral bonds per unit cell to the number of electrons appropriate for the skeletal bonding of the polyhedron.

As follows from the previous analysis, the effect on the frontier e bands of the delocalization through the π-interactions will be larger when the number of linking directions increases. In other words, for a given polyhedral unit cell, we should expect a decrease of the energy gap when the dimensionality of the infinite system increases. This is in agreement with the results of Figure 2 where we have collected the energy gap and overlap populations for some of the vertex-linked systems we have considered. Another corollary of the previous discussion is that there should always be two types of M–M links broadly differing in the bond strength, i.e., the interpolyhedral (electron precise) bonds should be noticeably stronger than the intrapolyhedral (electron-deficient) ones. This is again in agreement with the results of Figure 2, which reports results for systems built with identical inter- and intrapolyhedral bond distances. It is also in excellent agreement with the experimental structures for these types of systems. For instance, the inter-/intrapolyhedral distances in CaB_6 and YB_{12} are

1.667/1.752 Å and 1.684/1.809 Å, respectively.[22]

A parameter we will find useful later is N, the number of electrons per boron or gallium atom required by the electronic structure of a particular geometrical arrangement. We use the parameter N_f to measure the number of electrons per boron or gallium atom in a given fragment of the structure. We will use another parameter, N_F, to indicate the number of electrons per boron or gallium atom required by the observed stoichiometric formula of the compound. If a given solid is made up of one type of fragment only then clearly $N_F = N_f$. CaB_6 is an example of this type. With vertex-linked closo octahedra $N = N_f = 20/6 = 3.33$. For nido octahedra linked in the same manner to give the three-dimensional structure (**14**) $N = N_f = 19/5 = 3.80$. This structure is unknown. We will show below why it is an unlikely choice for an $M^{IV}B_5$ material, even though this electron count perfectly satisfies the electron-counting rules for this geometry.



14

Table I shows a selection of examples with vertex-linked deltahedra and the electron-counting procedure. Each four-coordinate spacer requires four electrons and each three-coordinate spacer three electrons for bonding. The dimer in the MB_4 structure contains a B=B double bond and so requires eight electrons to satisfy its bonding requirements. Figure 3 shows a total and partial density of states for this system which nicely shows the π-bond. The CBC trimer in "B_4C" presents some counting problems, but Longuet-Higgins and Roberts assigned 10 electrons to it.[20] This material has variable stoichiometry, and the electron count is analogously variable around 47 electrons per formula unit.

The electron counting is not always perfect. Sometimes this is a result associated with the experimental difficulties in the exact determination of the stoichiometry. In the system initially identified as "Li_3Ga_{14}", for example,[24] there are icosahedra linked by isolated atoms arranged so as to require 138 electrons per cell. Only 135 are present. In a more recent structural determination by the original authors[25] the system has been reassigned as Li_2Ga_7 (Li_4Ga_{14}) which fits the counting rules perfectly (Table I). Another example, but one where the structure and stoichiometry appear correct, is the CaB_6 structure observed for KB_6. Here the

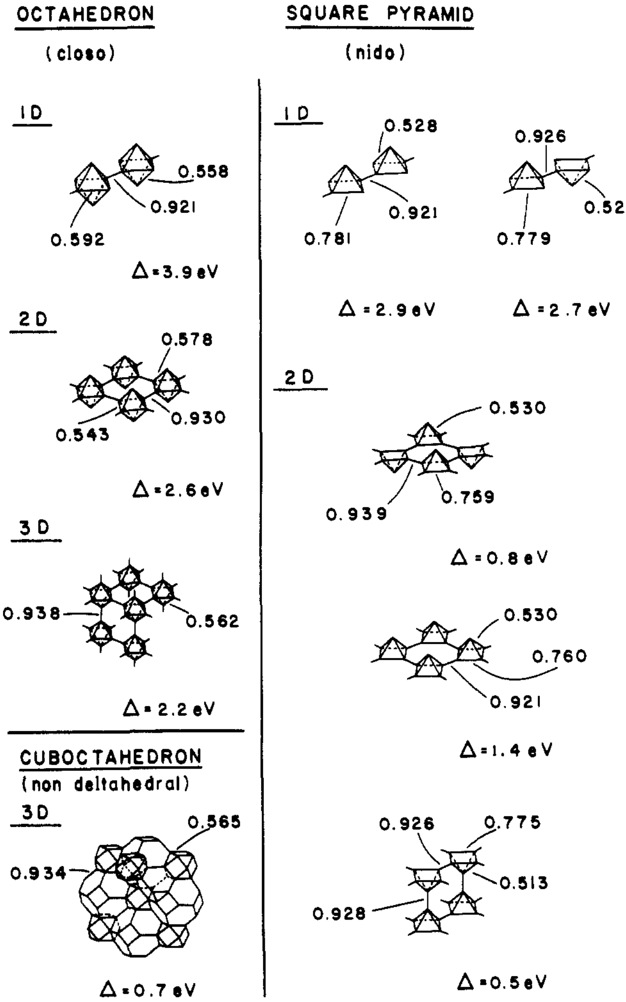


Figure 2. Overlap populations and band gaps for some vertex-linked polyhedral infinite systems. Calculations were actually done by using boron as the main-group atom and identical inter- and intrapolyhedral distances.

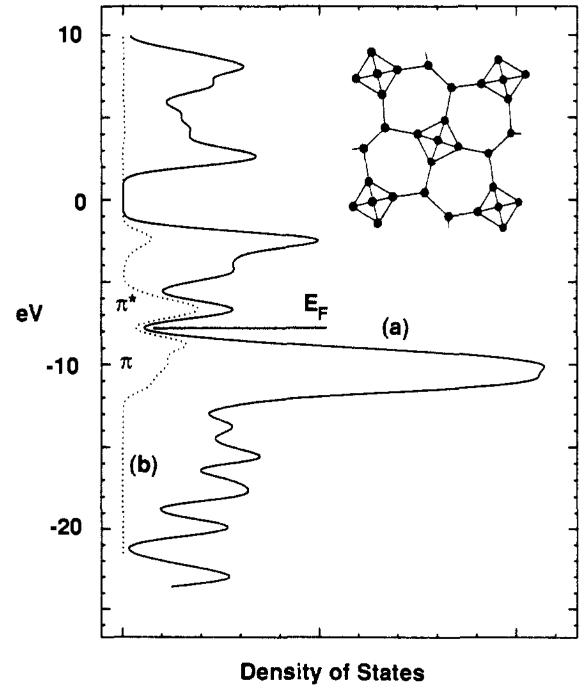


Figure 3. (a) Total density of states for the MB_4 structure. (b) Projection of the π density associated with the linking dimer. The Fermi level is shown which nicely separates the π and π* levels of the dimer. (Calculation courtesy of Paul Czech.)

---

(21) La Placa, S.; Binder, I.; Post, B. J. *Inorg. Nucl. Chem.* **1961**, *18*, 113.

(22) (a) See: Hoard, J. L.; Hughes, R. E. In *The Chemistry of Boron and Its Compounds*; Muetterties, E., Ed.; Wiley: New York, 1967; p 25. (b) Although strictly speaking the YB_{12} structure contains one electron more than needed, this does not affect the discussion because the extra electron goes into a mainly localized metal d orbital. A similar comment is true of LaB_6.

(23) (a) Mair, G. Thesis, University of Stuttgart, 1984. (b) Mair, G.; Nesper, R.; von Schnering, H. G. *J. Solid State Chem.* **1988**, *75*, 30.

(24) (a) Belin, C.; Ling, R. G. *J. Solid State Chem.* **1982**, *45*, 290. (b) Stöhr, J.; Schäfer, H. *Rev. Chim. Min.* **1982**, *19*, 122.

(25) Tillard-Charbonnel, M.; Belin, C. *C. R. Acad. Sci. Ser. B* **1988**, *306*, 1161.

Table I. Electron Counting for Vertex-Linked Deltahedra

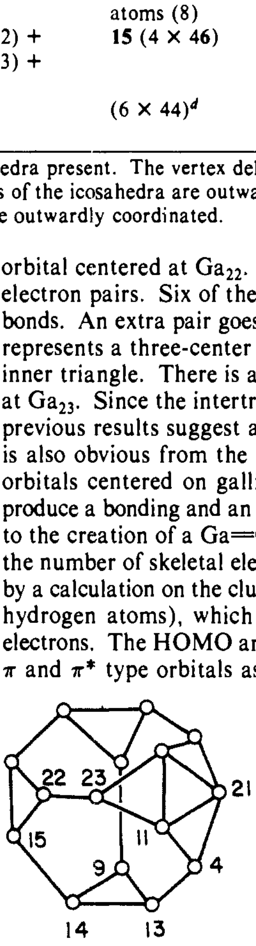
formula	structural formula[a]	electronic requirements				total from formula	ref
		skeletal electrons	exo bonds	spacer	total		
CaB_6, LiB_3	$Ca(B_6)$, $Li_2(B_6)$	14	6	none (0)	20	20	22a, 23a
KGa_3	$K_3(Ga_8)(Ga)$	18	8	4-coord atom (4)	30	30	11
$M^{II}B_4$	$M^{II}_2(B_6)(B_2)$	14	6	dimer (8)	28	28	22a
B_4C	$(B_{12})(CBC)$	26	12	trimer (10)	48	47	22a
Li_2Ga_7	$Li_{12}(Ga_{12})_3(Ga)_6$	78	36	4-coord atom (24)	138	138	24, 25
Li_3B_{14}	$Li_{24}(B_8)_4(B_{10})_8$	$(4 \times 18) +$ (8×22)	$(4 \times 8) +$ (8×10)	none (0)	360	360	23b
K_3Ga_{13}	$K_{24}(Ga_{12})_4(Ga_{11})_4Ga_{12}$	$(4 \times 26) +$ (4×24)	$(4 \times 12) +$ (4×11)	3,4-coord atoms (44)	336	336	26
Mg_2B_{14} $Mg_{0.5}AlB_{14}$	$Mg_2(B_{12})(B)_2$	26	12	4-coord atoms (8)	46	46	27
$Na_{22}Ga_{39}$	$Na_{88}(Ga_{12})_8(Ga^{b}_{15})_4$	(8×26)	$(8 \times 12) +$ $(4 \times 13) +$ 12^{c}	**15** (4×46)	552	556	28
Na_7Ga_{13}	$Na_{126}(Ga_{12})_{12}(Ga^{d}_{15})_6$	(12×26)	$216 +$ 36^{c}	$(6 \times 44)^{d}$	828	828	29

[a] All of the formulas are written here to emphasize the nature of the deltahedra present. The vertex deltahedra represented in the table are 8, 10, 11, 12, and 15. [b] The spacer is **15**. [c] Lone pair electrons. Not all of the atoms of the icosahedra are outwardly coordinated. [d] The spacer is the Ga_{15} cluster **15** where the Ga_{22} and Ga_{23} atoms do not form a double bond but are outwardly coordinated.

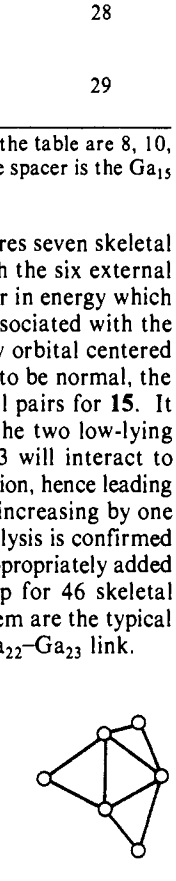
electron count is short by one electron per formula unit. A third example concerns materials with the Mg_2B_{14} structure. Although the parent species fits the scheme well, species are known with the same structure but with a stoichiometry $Na_xB_{0.84}B_{14}$ ($1 > x > 0.72$) which do not fit the scheme well. In this series the first boron sits in an interstitial site, and the structure seems to remain unchanged as sodium is removed from the material.[27]

An interesting rather complex "spacer" (**15**) is found in the structure of $Na_{22}Ga_{39}$.[28] Eight vertex-linked icosahedra and four such 15 atom spacers are found per unit cell. Not all of the icosahedra are 12-coordinate to their neighbors, so when counting electrons we have to take into account the "lone pairs" present at these uncoordinated sites. Atoms 22 and 23[30] are three-coordinate in $Na_{22}Ga_{39}$ but are outwardly coordinated to other gallium atoms in the closely related phase Na_7Ga_{13} ($Na_{21}Ga_{39}$).[29] The structue of this spacer unit is interesting. Schäffer[16] assigned 44 skeletal electrons to it; 21 two-center two-electron bonds and one closed three-center two-electron bond at the very top. The gallium-gallium linkage 22-23 is "normal" in $Na_{21}Ga_{39}$ (2.54 Å), but in $Na_{22}Ga_{39}$ it is however quite short (2.43 Å) compared to typical Ga–Ga distances associated with two-center two-electron bonds. A molecular orbital calculation shows it to be Ga=Ga, the first example of a homoatomic double bond with this element as far as we are aware. Belin and Ling[15] assigned 43 electrons to the skeletal bonding and considered each of the two atoms 22 and 23 as bearing a lone pair. King[31] considered the 22–23 linkage as a double bond and assigned 47 electrons (including the double bond) to the skeletal bonding. Although the last two counting schemes lead to the same number of total electrons for the spacer, the basis for these assignments does not seem to be quite firm. In addition, they disagree with Schäfer's counting. In view of this situation we decided to carry out a molecular orbital study of **15**.

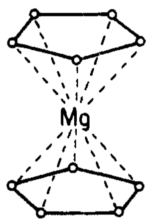
Some of the distances in the triangles of **15** are quite long, and this can lead to some problems in the electron counting. In consequence, we performed calculations on the three different triangular clusters present in **15**, where hydrogens were used to "saturate" the appropriate atoms. According to our calculations both the (15–22–15) and (14–13–9) clusters, require three skeletal electron pairs. In addition, the first one has a very low-lying empty orbital centered at Ga_{22}. The cluster **16** requires seven skeletal electron pairs. Six of them are associated with the six external bonds. An extra pair goes into an orbital higher in energy which represents a three-center two-electron bond associated with the inner triangle. There is also a low-lying empty orbital centered at Ga_{23}. Since the intertriangular bonds seem to be normal, the previous results suggest a total of 22 σ skeletal pairs for **15**. It is also obvious from the present results that the two low-lying orbitals centered on gallium atoms 22 and 23 will interact to produce a bonding and an antibonding combination, hence leading to the creation of a Ga=Ga double bond and increasing by one the number of skeletal electron pairs. This analysis is confirmed by a calculation on the cluster **15** (again with appropriately added hydrogen atoms), which shows an energy gap for 46 skeletal electrons. The HOMO and LUMO of the system are the typical π and π^* type orbitals associated with the Ga_{22}–Ga_{23} link.



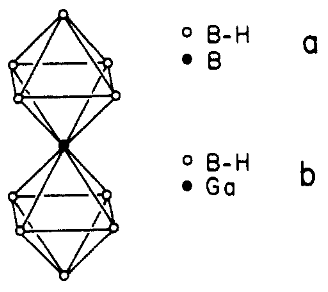
15



16



17



18

Thus the present analysis suggests that 44 and 46 are the appropriate number of skeletal electrons to be associated with the Ga_{15} clusters of Na_7Ga_{13} and $Na_{22}Ga_{39}$, respectively. This is in complete agreement with the Schäfer[16] viewpoint but disagrees with the Belin[15] and King[31] assignments. However, whereas the total number of electrons derived from the stoichiometry and the theoretical analysis (see Table I) match perfectly in the case of

---

(26) Belin, C. *Acta Crystallogr.* **1980**, *B36*, 1339.

(27) Naslain, R.; Guette, A.; Hagenmuller, P. J. *Less-Common Met.* **1976**, *47*, 1.

(28) Ling, R. G.; Belin, C. *Acta Crystallogr.* **1982**, *B38*, 1101.

(29) Frank-Cordier, U.; Cordier, G.; Schäfer, H. *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **1982**, *37*, 119.

(30) In **15** and the following discussion, the original numbering used in the X-ray structure determination[28] is used.

(31) King, R. B. *Inorg. Chem.* **1989**, *28*, 2796.

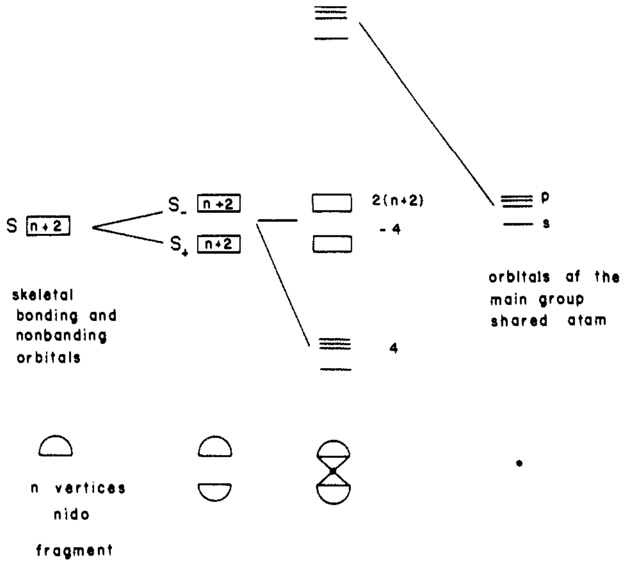


Figure 4. Schematic interaction diagram for vertex sharing of two closo fragments.

Na_7Ga_{13}, this is not the case for $Na_{22}Ga_{39}$. There are 556 electrons per unit cell, but the calculated number required is only 552. We note however some problems in the refinement of the $Na_{22}Ga_{39}$ structure associated with the sodium atoms.[28] We suspect, as was the case for Li_3Ga_{14}, that the stoichiometric formula of $Na_{22}Ga_{39}$ may be incorrect. According to our electron-counting scheme, this phase should be formulated as $Na_{21}Ga_{39}$ (i.e., Na_7Ga_{13}). Indeed Schäfer et al.[32] found a second Na_7Ga_{13} phase (Na_7Ga_{13}-II) which is practically identical with $Na_{22}Ga_{39}$ except for the sodium content.

In several systems the deltahedra are linked by three-center two-electron bonds in addition to the two-center two-electron ones described above. Longuet-Higgins and Roberts[20] described the α-rhombohedral boron structure in these terms, and Belin and Ling[15] interpreted the electronic structure of $RbGa_7$ in this way by noting the proximity of two extra-deltahedral atoms to some of the atoms forming the icosahedra in the structure. Here there are also isolated four-coordinate atoms in the structure.

Vertex-Fused Systems. These are not very common in either molecular main-group systems or in extended solids. **17** shows the structure of $MgCp_2$ which may be regarded as two vertex-fused nido pentagonal bipyramids.[33] CpIn can be considered an example of an infinite one-dimensional system.[34] In solids there are sometimes examples of defect deltahedra linked by an electropositive atom. Li_5Ga_9, for example, contains two nido icosahedra joined by a lithium atom.[25,35] The rules for electron counting here are simply derived from the condensation of two nido units around a single atom (Figure 4). Whatever the actual geometry of the condensed cluster (eclipsed or staggered nido units, heteroatoms present or not in the nido fragments, etc.) the four s and p orbitals of the shared main group atom always find a match with some of the S_+ or S_- skeletal orbitals. As a result, the filled orbitals of each nido unit interact with the four valence orbitals of the fusing atom to give the same electron count as the sum of the two parents. In this way their behavior is similar to that of an interstitial atom in a cluster.

There are, however, some subtleties associated with this process as we now show. Figure 5 reports the calculated energy levels for some apical vertex-shared octahedral systems. The number of skeletal electron pairs (SEP) have been assigned by counting the number of electrons needed to fill all bonding and nonbonding orbitals taking the energy of a 2p orbital on boron as the reference. Although 14 SEP are needed for **18b**, only 12 SEP are needed for **18a**. In other words, the rule illustrated in Figure 4 seems to work for **18b** but not for **18a**. The reason is simple. Implicit in Figure 4 is the fact that the direct interaction between the two nido fragments is small. This is certainly the case when the shared atom is larger than the atoms in the nido fragments. However when the shared atom is of the same nature as those in the basis of the nido fragments, the nido–nido interactions are not negligible, and some orbitals can interact strong enough to eject some of the S_- orbitals to the antibonding energy region. Conversely some empty levels of the parent fragments can be lowered to the nonbonding region. All these complications are illustrated in Figure 5. Twelve SEP are required for the dimer (**18a**) because two levels which are filled in the nido fragment have been raised above the nonbonding limit. Thus it could be tempting to generalize this result and consider that for this type of vertex-shared octahedral homoatomic clusters the number of SEP needed should be $(7m - 2(m - 1))$, where $m = 2$ for the dimer, 3 for the trimer, etc. However, this is not the case, because according to our calculations the only energy gap (2.3 eV) for the trimer corresponds to 19 SEP. As is obvious from Figure 5, the origin of this new algorithm for the SEP counting is that a pair of degenerate orbitals, descending from the empty orbitals of the parent fragment, reaches the nonbonding zone. Thus the SEP formula becomes $(7m - 2(m - 1)) + 2$. The two sets of highest occupied levels cross from the trimer to the tetramer, but the number of SEP is 24, just that predicted by the last formula. However, we note that the HOMO–LUMO gap is decreasing (1.3 eV). Another degenerate pair is coming down in energy, whereas the highest occupied nondegenerate level is going up in energy. In fact what we are describing is nothing more than the building of the bottom and top parts of the dispersive degenerate and nondegenerate bands of the infinite system (see Figure 5). These two bands strongly overlap in the polymer, a fact which should not confer a high stability to this system.

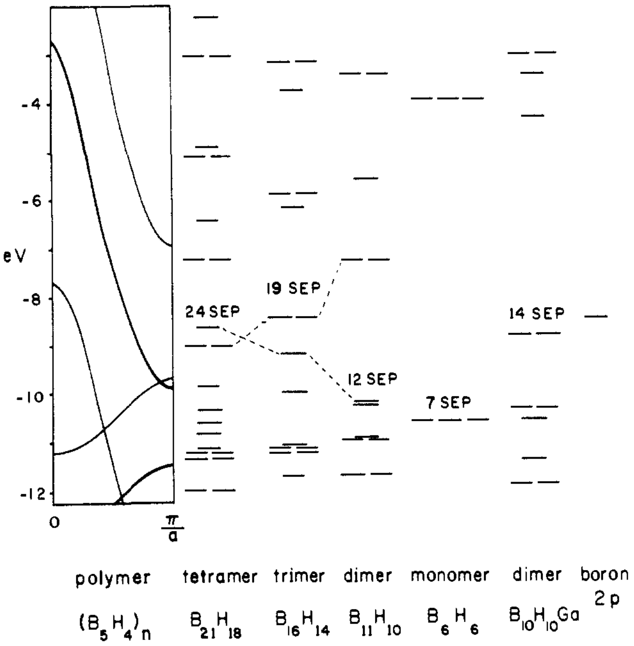


Figure 5. Energy levels for several apical vertex-sharing octahedral systems. Also included are the energy levels for a single octahedron as well as the energy of a boron 2p orbital. Thick and thin lines in the band structure represent doubly degenerate and nondegenerate bands, respectively.

The number of levels which can be ejected out of or pushed into the bonding/nonbonding region can depend quite subtly on the nature of the actual energy levels in the fragments themselves. For instance, for the apical vertex-shared dimer built from two square pyramids, two electron pairs should be subtracted from the sum of the SEP of the two arachno fragments but three for apical vertex sharing of two pentagonal pyramids. In addition

---

(32) Frank-Cordier, U.; Cordier, G.; Schäfer, H. *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **1982**, *37*, 127.

(33) Eisenstein, O.; Canadell, E.; Thanh, B. T. *Nouv. J. Chim.* **1986**, *10*, 421.

(34) (A) Frasson, E.; Menegus, F.; Panattoni, C. *Nature (London)* **1963**, *199*, 1087. (b) Canadell, E.; Eisenstein, O.; Rubio, J. *Organometallics* **1984**, *3*, 759.

(35) Belin, C. *Rev. Chim. Min.* **1984**, *21*, 263.

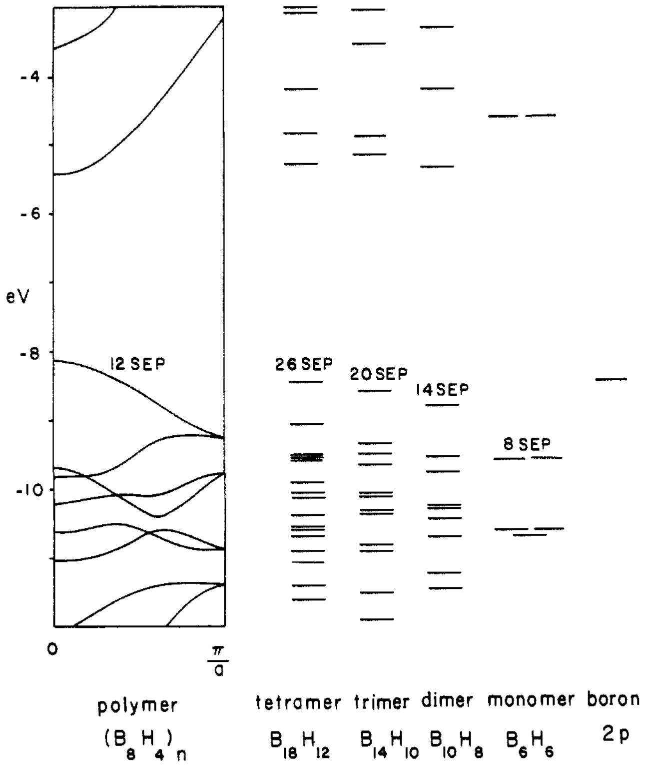
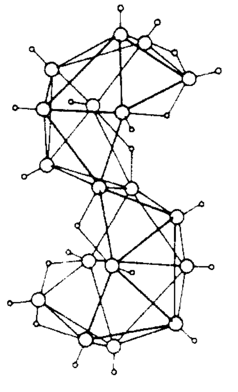


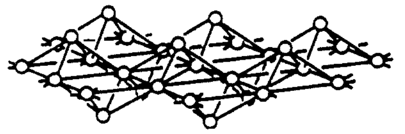
Figure 6. Energy levels for the dimer, trimer, and polymer built from edge fusing of pentagonal pyramids. Also included are the energy levels for a pentagonal pyramid and the energy of a boron 2p orbital.

to the number of vertices, heteroatom substitution of selected atoms or changes in the pyramidalization of some centers can also lead to changes in the SEP. It is not our purpose to consider this interesting problem in detail here but only to point out some of the results suggested by our calculations. First, it is clear that a single formula is inappropriate for these main-group homoatomic vertex-shared clusters. In particular, the formulas derived by Teo[7] and Mingos[3] are not applicable to these cases. Second, if the vertex-shared atoms are larger than the unshared ones, the appropriate number of SEP is simply the sum of those of the parent fragments. Recent examples of this class of compounds have been reported by Hawthorne[36,37] and Cowley.[38] Third, our calculations suggest that main-group homoatomic vertex-shared infinite systems should not be especially stable. Although there can be other factors at play, this is undoubtedly one of the reasons why these systems have not been observed. Fourth, the variety of factors which can influence the appearance of an energy gap suggest that some interesting molecular chemistry is yet to be done in this area.

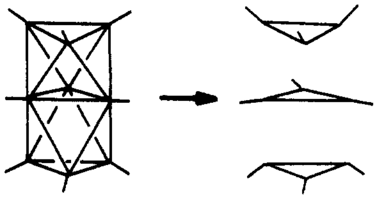
Edge-Fused Systems. Edge-fused species occur in both molecular chemistry (e.g., **19**[39]) and in extended arrays. The structure of MgB_4 consists of one-dimensional chains of edge-sharing nido pentagonal bipyramids (**7**) vertex-linked into a three-dimensional structure.[12] The structure shown in **20** can be regarded as a two-dimensional sheet made up of nido octahedra. PbO has a structure similar to this, but here the pyramids are flattened so that there are long distances between the basal atoms of the pyramid. Again with long interbasal linkages it is found for $BaAl_4$. Both of these structures have been studied theoretically.[40,41] However, because of the elongation of the basal linkages these systems should not be considered as condensed deltahedra. In fact the only extended system built from edge-shared deltahedra of which we are aware is MgB_4.



19



20



21

Our results for several edge-shared pentagonal pyramid systems are shown in Figure 6. In these and the following calculations the apical atoms were set alternatively up and down the basal planes as shown in **7**. The number of appropriate SEP is simply given by the formula $8m - 2(m - 1)$ where m is the number of pentagonal pyramids in the structure. A very sizable gap is found all along the condensation process including the polymer (2.7 eV). It is then quite clear that these systems should be quite stable. In the MgB_4 structure[12] the chains **7** are vertex-linked to other chains through the two unshared atoms so that a total of 14 electrons per formula unit are needed according to our calculations (12 for intradeltahedral bonding and two for two-center two-electron extradeltahedral bonding). This is exactly the number derived from the chemical formula.

Since there is both theoretical and experimental support for this counting, it is interesting to compare our results with those of the topological electron counting rules developed by Teo.[7] These rules give equations for the total number of electron pairs P associated with structures in terms of the number of faces F, vertices V, and a constant X, dependent upon the mode of fusion or linking. For main group systems The parameter X has to

$$P = 3V - F + 2 + X$$

be determined separately by using a set of rules developed by Teo. The value for any pyramidal system is 0. Once the value for X has been determined for a polyhedron, edge fusion results in an increase equal to the number of shared edges with respect to the sum of the values associated with the separate polyhedra. Thus for the pentagonal pyramid $\{V, F, X\} = \{6, 6, 0\}$ and $P = 14$. Of these there are clearly six outward pointing bonds and thus $V + 2 = 8$ skeletal electron pairs. However, for the edge-sharing of two pentagonal pyramids $\{10, 12, 1\}$ the total electron count is 21 pairs compared to the 22 pairs calculated here. As was the case for vertex-shared clusters, the rules do not work for main-group systems.

---

(36) Schubert, D. H.; Rees, W. S.; Jr.; Knobler, C. B.: Hawthorne, M. F. *Pure Appl. Chem.* **1987**, *59*, 869.

(37) Bandman. M. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1988**, *27*, 2400.

(38) Siriwardane, U.; Islam, M. S.; West, T. A.; Hosmane, N. S.; Maguire, J. A.; Cowley, A. H. *J. Am. Chem. Soc.* **1987**, *109*, 4600.

(39) Simpson, P. G.; Folting, K.; Dobrott, R. D.; Lipscomb, W. N. *J. Chem. Phys.* **1963**, *39*, 2339.

(40) (a) Burdett, J. K.; Lin, J.-H. *Acta Crystallogr.* **1981**, *B37*, 2123. (b) Trinquier. G.; Hoffmann, R. *J. Phys. Chem.* **1984**, *88*, 6696. (c) Burdett, J. K.; Miller, G. J. *Chem. Mat.* **1990**, *2*, 12.

(41) Zheng, C.; Hoffmann, R. *Z. Naturforsch.* **1986**, *41B*, 292.

The number of SEP to be substracted from the sum of the SEP of the parent deltahedra changes with the nature of the polyhedron. For instance when we repeated the calculations of Figure 6 by using square pyramids, the number of SEP found were 7, 10, and 13 for the monomer, dimer, and trimer, respectively. The number to be subtracted here is then not two but four. Another very important difference compared to the case of pentagonal pyramids is that the gap decreases very rapidly on polymerization and eventually disappears (5.4 ev in the monomer, 3.0 in the dimer, 1.5 in the trimer). The polymer shows broadly overlapping bands. The difference compared with the previous case lies in the low symmetry of the pentagonal pyramid systems compared with those of the square pyramid series. This allows the mixing of orbitals which tend to be lowered/raised by the fusion process in the first case but not in the second. For pyramids with an even greater number of basal atoms we can then predict that the edge-fusing process leading to the less symmetrical cluster will be generally preferred.

This situation is more complex when the geometrical constraints of the edge fusion result in short nonbonded atom–atom contacts. For instance this is the case for octahedral edge fusion. Here the apical–apical interactions lead to problems similar to those printed out in the previous section: somewhat erratic behavior of the SEP numbers, small gaps in many cases, and broadly overlapping bands in the polymer. A simple formula for the SEP is clearly inappropriate. Again the actual number of SEP can be altered by a number of factors. The nature of the ligands around the shared atoms (normal and bridging) and local distortions such as those found in transition-metal oxides with edge-fused octahedral chains[42] are both important. In conclusion, our study suggests that there are quite strong geometrical and symmetry factors limiting the electronic stability of edge-fused main-group systems and especially extended arrays. It is quite remarkable that the simple rules do not apply to the only characterized system of this type.

Face-Sharing Deltahedra. Face-sharing units are found in some of the gallium phases examined by Belin and co-workers. **8** shows the structure of two face-sharing icosahedra found in $Rb_{0.6}Na_{6.25}Ga_{20.02}$.[13] The sites 11 and 29 are not completely occupied (81% and 51%, respectively) so that nido, arachno, and in principle other even more defective deltahedra are present. Similar units are found in $Li_3Na_5Ga_{19.6}$[43] and $K_3Li_9Ga_{28.83}$.[44] In $K_4Na_{13}Ga_{49.57}$ a triply-fused icosahedron is found.[14]

The simplest case of face-sharing arises when one of the deltahedra is a tetrahedron. This really corresponds to the capping of a triangular face of the larger deltahedron by a single atom. The electron-counting rule for capped deltahedra is a very simple one: *n* vertices including the cap and *n* skeletal pairs of electrons. The rule works well in practice and may be readily understood since the three outward pointing orbitals of the capped face find exact orbital matches with the frontier orbitals of the capping fragment, and the skeletal electron count for the new polyhedron is the same as for the old. The state of affairs becomes more complex for the face-sharing of other deltahedra. We will not be exhaustive in our discussion but will study systems which are chemically realistic.

In Figure 7 we report the energy levels for a series of face-shared octahedral systems. Although these clusters have not yet been prepared with group 13 elements, many of them as well as the infinite chain are known as ternary molybdenum chalcogenides.[45] They present very interesting physical properties. As can be seen from Figure 7, all of them have quite important energy gaps. There is also a band gap in the polymer. The number of SEP appropriate for these systems is 10 for the dimer, 13 for the trimer, etc. Clearly, the number of SEP can be generated by substrating 4 from the sum of those of the parent polyhedra before fusion.

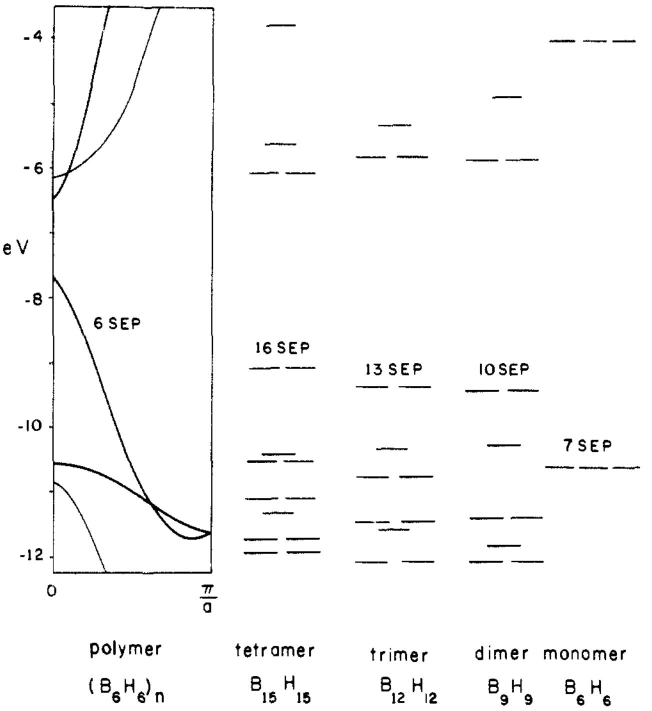


Figure 7. Energy levels for several face-sharing octahedral systems. Thick and thin lines in the band structure represent doubly degenerate and nondegenerate bands, respectively.

The origin of this behavior can be understood by considering a fused system as a series of "inner" planar $(MH)_3$ triangles capped at the top and bottom by $(MH)_3$ triangles somewhat pyramidalized. This is illustrated in **21** for the dimer. The skeletal bonding of each triangle is characterized by three σ and one π (π_1) orbitals. The other two π orbitals ($\pi_{2,3}$) remain at higher energies. When assembling the dimer from the three sets of orbitals, the mixing between σ- and π-type orbitals is very strong—this is how multicentered electron-deficient bonding appears—so that the interaction diagram looks quite complex. For electron counting however the procedure is very simple. The in-phase combination of "capping" π_1 orbitals strongly interacts with the inner π_1 and is ejected to the antibonding region. The second combination cannot interact with the inner π_1 but interacts quite strongly with σ ones of the inner triangle (**22** and **23**) and is also ejected (**24**). In short, only one combination of π_1 orbitals remains occupied. The $\pi_{2,3}$ orbitals are kept high in energy because in all of their combinations, antibonding interactions between the π orbitals of one triangle and the σ ones of the nearest triangle are allowed. We insist that the π–σ mixing is strong, but the essential result for electron counting purposes is kept in the schematic diagram of **24**. The procedure can be easily generalized to any system of this series (or even to the octahedron itself): in all cases there are enough nearest triangle π–π and π–σ interactions to leave empty all π-based orbitals except the most bonding one and to leave occupied all the σ-based ones. Formally, any new member of the series can be generated by adding a set of three SEP to the parent system as actually found in the calculations.

How do the results of Figure 7 compare with Teo's scheme? From octahedron {6, 8, 1} to face-sharing bioctahedron {9, 14, 2} the required total number of pairs predicted changes from 13 (seven skeletal) for the octahedron (correct) but 17 pairs for the fused unit. Our calculations show that 19 pairs is the correct Figure. For the fused octahedral trimer our calculations show that 25 pairs are needed; Teo's rule gives 21. There is thus an error in Teo's scheme of two pairs per fusion when applied to these main-group systems.

Teo's rule seems to work for the face fusion of two icosahedra. Our calculations for **8** (using boron atoms) show that 23 is the appropriate number of SEP. The new deltahedron has three fewer vertices and two fewer faces. The rule for generating the X value

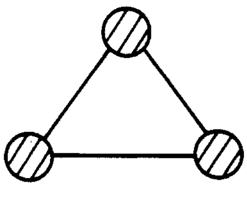
---

[42] Mc Carley, R. E. In *Inorganic Chemistry: Towards the 21st Century*; ACS Symposium Series; American Chemical Society: Washington, DC, 1982, pp 273–90.

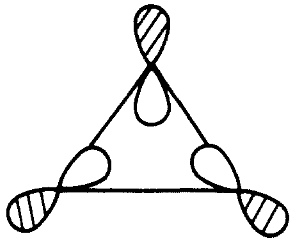
[43] Charbonnel, M.; Belin, C. *Nouv. J. Chim.* **1984**, *8*, 595.

[44] Belin, C. *J. Solid State Chem.* **1983**, *50*, 225.

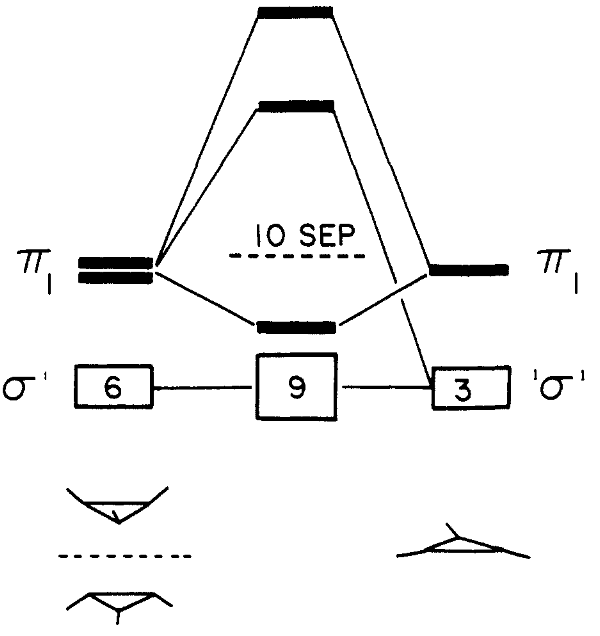
[45] Chevrel, R.; Gougeon, P.; Potel, M.; Sergent, M. *J. Solid State Chem.* **1985**, *57*, 25.



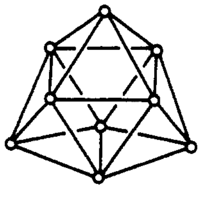
22



23



24



25

for the fused system involves simple addition of the X numbers for the individual units. Thus for {21, 28, 14} a total of 41 electron pairs or 23 skeletal pairs are needed for stability. However, we suspect the agreement is fortuitous. It should be noted that during the fusion process three short M–M distances between atoms of different icosahedra are generated (see **8**). These contacts were indeed found very short in $Rb_{0.6}Na_{6.25}Ga_{20.02}$ where these polyhedra were characterized. A detailed analysis of the electronic structure of this system shows these contacts to have a strong influence on the final SEP number. Indeed this is not the only complicating feature of these systems. Partial occupancy of several sites in the observed structures makes the electron counting somewhat more complex. The structures and electronic requirements of some of these complex large defective deltahedra will be described elsewhere.

Another interesting system is the tricapped triangular prism (TTP), **25**. It is an isomer of the face-sharing octahedron. Successive face sharing of the prismatic bases generates isomers of the face-shared octahedral systems. Exactly the same number of SEP are needed for the TTP and face-shared octahedra B_9H_9. The gap is, however, 1.2 eV smaller in the former. Fusion of the TTP results in very short distances between capping atoms which lead to no clear energy gaps for the members of this series. The polymer shows broadly overlapping bands, and we did not find a simple distortion leading to a band gap. Face sharing of octahedra should be a more likely alternative for all these systems.

Table II. Electron Concentration per Atom for Various Units[a]

electron concentration in the fragment per atom, (N_f)	structural unit	example
3.00	face, vertex, and edge sharing octahedra	fcc Al
	face-sharing octahedral polymer	none
	vertex-linked closo icosahedra with two-center two-electron and three-center two-electron bonds	elemental boron
3.05	face-sharing closo icosahedral dimer	$Li_3Na_5Ga_{19.6}$
3.13	face-sharing octahedral tetramer	none
	closo 15-vertex Δ[b]	BeB_3
3.15	face-sharing nido icosahedral dimer	$Li_3Na_5Ga_{19.6}$
3.17	face-sharing octahedral trimer	none
	vertex-linked closo icosahedra	many
3.18	vertex-linked closo 11 vertex Δ	K_3Ga_{13}
3.20	vertex-linked closo 10 vertex Δ	Li_3B_{14}
3.22	face-sharing closo octahedra dimer	none
	vertex-linked closo 9 vertex Δ	none
3.25	vertex-linked closo 8 vertex Δ	KGa_3
3.26	face-sharing arachno 12 vertex dimer	$Li_3Na_5Ga_{19.6}$
3.29	vertex-linked nido 15 vertex Δ	SiB_6
	vertex-linked closo 7 vertex Δ	none
3.31	vertex-linked cis arachno 15 vertex Δ	SiB_6
3.33	vertex-linked closo octahedra	CaB_6
3.36	vertex-linked nido 12 vertex Δ	many
3.39	face-sharing hypho 12 vertex dimer	$K_3Li_9Ga_{28.83}$
3.40	vertex-linked nido 11 vertex Δ	none
3.42	vertex-linked closo 12 vertex Δ with three lone pairs	Na_7Ga_{13}
3.44	vertex-linked nido 10 vertex Δ	none
3.46	vertex-linked trans arachno 15 vertex Δ	SiB_6
3.50	edge-sharing nido 7 vertex polymer	MgB_4
	vertex-linked cis hypho 15 vertex Δ	SiB_6
	vertex-linked nido 9 vertex	none
3.53	face-sharing superhhypho 12 vertex dimer	none
3.57	vertex-linked nido 8 vertex Δ	none
3.60	vertex-linked arachno 12 vertex Δ	none
3.64	vertex-linked nido 12 vertex Δ with three lone pairs	none
3.66	vertex-linked nido 7 vertex Δ	none
3.80	vertex-linked nido octahedron	none
3.90	vertex-linked arachno 12 vertex Δ with three lone pairs	none
4.00	vertex-linked arachno 8 vertex Δ	none
4.20	vertex-linked arachno 7 vertex Δ	none
4.25	vertex-linked arachno octahedra	none

[a] This tabulation is by no means exhaustive. [b] The symbol Δ is used for the word deltahedron.

The face-sharing octahedral polymer, while probably not a candidate for a new form of boron, as we describe later, could be stable for a material of stoichiometry $(BH)_n$. While boron polymers of this type are presently uncharacterized, we recall the yellow solid often left behind in vacuum lines through which boranes have passed.

The Structure of Electron-Deficient Materials. At this stage we may draw together many of the ideas we have presented earlier concerning these structures. What are the factors which determine the structures of species with between three and four electrons per framework atom? We know that the detailed reasoning will be complex, but electron count seems to be an important factor as we now show.

First we point out the relative energetic preferences for three- and six-membered rings in structures as a function of electron count. As we have earlier illustrated by using the method of moments,[46] between three and four electrons per atom, the preference for three-membered rings (well established at three electrons) is replaced by that for six-membered rings (well established at four electrons). Table II shows the electron concentration (N_f) for various building blocks of these structures. Interestingly we note that at N_f = 3.5 electrons per atom there appears to be a sharp cutoff concerning the observed stability of these units. No deltahedra (complete, fragmented, or fused) with

---

[46] Burdett, J. K.; Lee, S. *J. Am. Chem. Soc.* **1985**, *107*, 3063.

electron concentrations greater than $N_f = 3.5$ are observed. Since framework atoms are usual in these structures, the cutoff should be near but slightly greater than 3.5 when considering N_F. Thus, for example, the structure of Mg_2Ga_5 which has a gallium electron count from its formula of $N_F = 3.8$ electrons/atom is not found as the three-dimensional vertex-sharing nido octahedral structure (**14**) described earlier but as an opened up structure containing six-membered rings[47] (**26**). The Mg atoms are not shown in **26** for simplicity. At this point we recall the graphite-like structures found for several of these systems with $N_F = 4.0$. Thus MgB_2, $CaGa_2$, and LiBC have either the AlB_2 structure or a derivative which contains fused planar six-membered rings.[48] $CaIn_2$ may be regarded as an intercalated hexagonal diamond structure.[48] Here the indium net contains fused, puckered six-membered rings. For $N_F = 4.0$ the traditional Zintl ideas are strong ones.

$BaAl_4$ noted earlier with $N_F = 3.5$ electrons/atom lies at the boundary of three ring/six ring structures. It is, however, a structure which contains opened up nido octahedra which are linked to give six-membered ring structures. Since it does lie close to this boundary of 3.5 electrons/atom, it may be possible to make another form of $BaAl_4$ or by replacement of some of the Ba by Li move the electron count below this figure and stabilize a solid containing clusters.

Table II shows how the electron count per atom varies with the structural unit. Smaller electron counts are obtained by going to larger more complete deltahedra which share a large number of polyhedral elements. Larger deltahedra of course generally mean a less close-packed structure which may be energetically undesirable, but the increasing degree of deltahedral fusion leading to lower electron counts is easily seen in practice. As Zheng and Hoffmann[40] have pointed out the structure of fcc aluminum metal (with three electrons per atom) contains heavily polymerized octahedra, which, depending upon the vantage point, share vertices, edges, faces, or all three. An electron count of $N_f = 3$ electrons/atom is also found (Table II) for the face-sharing octahedral chain which is vertex linked to its neighbors. It is, however, difficult to imagine in geometrical terms how an infinite three-dimensional structure may be built up by using this one-dimensional building block. There appears then to be nothing wrong with its electronic stability, but geometrical factors, associated with the interchain contacts, may prevent its realization. (As we have commented above, as a BH polymer it could well be stable.)

The nido icosahedron becomes a more prevalent building block as the average atomic concentration N_F increases. Up to an average electron count of about $N_F = 3.28$ electrons/atom all of the icosahedra which are found are of the closo variety, such as those found in Li_2Ga_7 for example. At $N_F = 3.34$ electrons/atom in $Rb_{0.6}Na_{6.75}Ga_{20.02}$ nido icosahedra make their appearance. At the same time we find icosahedra which are less than 12-coordinate to their neighbors such that there are lone pairs of electrons at outward pointing sites. We note that $N_f = 4.0$ if 10 out of the 12 vertices are not linked to their surroundings. The critical value of $N_f = 3.5$ occurs if four of the vertices have lone pairs. This number is not reached in any of the deltahedra we have examined. Both of these features are ways to increase the electron count per atom for deltahedral stability. However, what is puzzling is the role of condensed deltahedra. These correspond to low electron counts (N_f) per atom but are only found in practice as the electron concentration increases above about $N_F \sim 3.33$ e/atom (in $Rb_{0.6}Na_{6.25}Ga_{20.02}$, for example, with an average electron concentration of $N_F = 3.34$ e/atom). These deltahedra are found in structures with several isolated atoms (requiring an electron count $N_f = 4.0$), the proportion depending upon the value of N_F itself. It appears that such condensed deltahedra are not capable of being efficiently packed together via vertex-sharing but need the geometrical flexibility of the framework atoms. The structures containing them will therefore have higher values of N_F than otherwise expected. The geometrical control of these structures is thus a strong one.

Table III. Parameters Used in the Calculations

	orbital	H_{ii}, eV	ζ[a]
B	2s	−15.20	1.30
	2p	−8.50	1.30
Ga	4s	−14.58	1.77
	4p	−6.75	1.55

[a] Slater-type orbital exponents.

The structural-electronic limitations on other structures should be somewhat more transparent given the rules and observations above. If the dodecahedron is regarded as a distorted cube, we could imagine a structure built from dodecahedra and isolated (tetrahedral) gallium atoms of stoichiometry $(Ga_8)Ga_2$ which would be the structural analogue of the fluorite structure. The vertex-linked Ga_8 dodecahedron has an N_f less than the critical cutoff of 3.5 and requires a total of $18 + 8 = 26$ electrons for stability. The two isolated gallium atoms require four electrons each, giving a desired total of 34. Only 30 are present from the gallium atoms themselves, and thus four more need to come from other atoms which would need to be inserted in the structure. It is not clear whether there is space in the arrangement we have described. Similar arguments lead to the prediction of an Al_2O_3 type of structure for vertex sharing octahedra as $(Ga_6)_2Ga_3$ with a calculated N of 3.464. These solids would have to occur for materials of stoichiometry $LiGa_{2.5}$ and $LiGa_{2.16}$, implying partial occupancy of some of the holes in the structure with lithium atoms. One interesting structure, which also illustrates the topological control of the structural-electronic problem, consists of vertex-linked dodecahedra alone. These require a value of N_f of 3.25 (Table II). To have the correct electron count a solid would have to correspond to a stoichiometry MGa_4. The possible structure is simply derived from the vertex-linked cube structure described in ref 46 by distortion of the cube to the dodecahedron. Such a structure contains holes between the cubes such that if all are filled a stoichiometry of M_3Ga_{16}, rather than MGa_4, is appropriate. For $M = M^I$, $N = 3.19$ and for $M = M^{II}$, $N = 3.38$, two figures far from those required for stability. Such a system may then adopt some other structure. $NaGa_4$ in fact adopts the $BaAl_4$ structure.

Another interesting observation of this section is the change from deltahedral to extended nondeltahedral-type structures occurring at N_F values around 3.5. In that respect the $Na_{22}Ga_{39}$ phase ($N_F = 3.56$, but remember our remarks before concerning a possible slightly lower N value) is extremely interesting. As we described before, this system contains both icosahedra and the spacer **15**. Nevertheless, in the three-dimensional framework, **15** is not located between icosahedra but is linked to other units **15** to form infinite chains. As we showed earlier **15** is an electron-deficient (although nondeltahedral) unit. In consequence, $Na_{22}Ga_{39}$ (with N_F near 3.5) contains both deltahedra and an extended electron-deficient nondeltahedral network.

With higher N_F values the deltahedra completely disappear. A pertinent example is Mg_2Ga_5. With $N = N_f = 3.8$ a three-dimensional framework of vertex-linked nido octahedra (see Table II) as shown in **14** could be a likely structure. The observed one[47] is completely different (**26**) with no deltahedra at all. The structural motif of the gallium framework is the Ga_{10} cage (**27**). A calculation for a $Ga_{10}H_{18}$ cluster, i.e., the cage **27** saturated with hydrogens, shows a gap of 3.6 eV for a total of 10 SEP. Four SEP are used to form the two-center two-electron vertical bonds of **27**. Three SEP are used to form the electron-deficient bonding in each of the two units **28**. How this number comes about is easy to see from the interaction diagram **29**. The counting in the solid is now easy. Each unit **27** forms 18 two-center two-electron external bonds with other units which require 18 electrons per **27**. Since the intracage bonding requires 20 electrons, this leads to 38 electrons per **27** unit, i.e., $N = N_f = 3.8$ for this structure. In other words, the electron deficiency has been taken care of in

---

(47) Smith, G. S.; Johnson, Q.; Wood, D. H. *Acta* Crystallogr. **1969**, *B25*, 554.

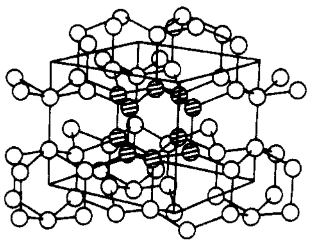
(48) Pearson, W. B. *The Crystal Chemistry and Physics of Metals and Alloys*; Wiley: New York, 1972.

(49) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

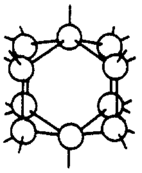
(50) Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093.

(51) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

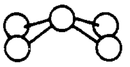
Mg_2Ga_5 without the creation of any deltahedra.



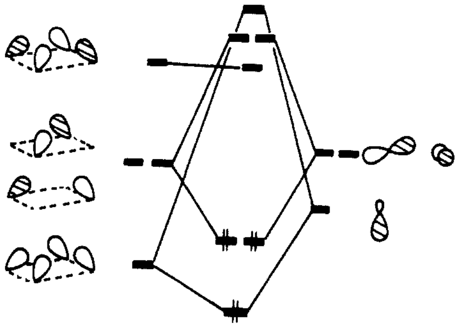
26



27



28



29

It is then vital to ask at this stage wy it is that in solids with N_F slightly larger than 3.5 deltahedral structures are not formed, but in molecules (such as the nido octahedral B_5H_9 with $N_f = 3.8$) such geometries are the rule for $N_f < 4$. The answer we believe is actually quite simple and has to do with the fundamental geometrical difference between molecular systems and extended solid-state arrays. The geometrical versatility of the latter is enormous, and it is often easy to see how six-membered rings may be built into the structure when electronically needed. In the molecule the geometrical restrictions are much tighter. In B_5H_9 for example, with $N_f = 3.8$, a six-membered ring of boron atoms is an impossibility for the monomeric molecule.

Boron–Gallium Differences. The most obvious difference between these two atoms of course, is their size which controls the dimensions of any framework generated by linking atoms together and also the size of the holes which will be present in such an arrangement. The different structures which are found illustrate the importance of such geometrical considerations. Within boron chemistry different structures are found for $M^{II}B_4$, that of MgB_4 with a small ion and that of YB_4 which can accommodate a larger ion. Although there are no structures known with the same stoichiometry and electropositive element, one observation we can make concerning the difference in structures found in borides and gallides is the occurrence of B_6 octahedra but the prevalence of gallium icosahedra and other icosahedral type (nido, arachno, fused, etc.) Ga_n units.

The origin of these preferences is a difficult problem to tackle because of the well-known problems arising in extended Hückel calculations when comparing situations with different coordination numbers. In these cases the total overlap population is usually the best indicator of structural stability. Indeed we have found that the total overlap population per atom is greater for an M_6H_6 octahedron in the case of boron (1.018 vs 1.002) but for an $M_{12}H_{12}$ icosahedron in the case of gallium (0.966 vs 0.932). This is in excellent agreement with the above observation. An analysis of the different contributions to the total overlap population shows that the icosahedron is preferred in both cases if *only* M–M bonded contributions are retained. Only when the nonbonded interactions are retained does the octahedron become the preferred polyhedron for boron. These nonbonded interactions are repulsive and quite sizable as commented on earlier. There are two bonds per atom in the octahedron but 2.5 in the icosahedron. Although the absolute values of these overlap populations are smaller in the icosahedron, the greater number of bonds dominates and makes the icosahedron preferred in both cases. However, there are only 0.5 nonbonded interactions per atom in the octahedron but 2.5 in the case of the icosahedron (we only retain the second nearest neighbor ones; there are six additional ones which are very weak in both cases). This great number of nonbonded interactions destabilizes the icosahedron with respect to the octahedron in the case of boron because of the less diffuse nature of the orbitals which makes the nonbonded interactions strong. For gallium the diffuseness of the orbitals makes their role less important. In other words, gallium which has more diffuse orbitals focuses on forming strong bonds, but boron, with more contracted orbitals, looks for a compromise between good bonding and small repulsive nonbonded interactions.

These observations, which qualify the intrinsic stability of different deltahedra for boron and gallium, can be important in understanding some of the exceptions we have mentioned earlier. For instance, KB_6, with the vertex-linked CaB_6 structure, has an N_F value (3.17) which corresponds to the N_f value for vertex-linked icosahedra. Since a three-dimensional network of this type is impossible on geometrical grounds, the system would have to adopt a structure with some framework boron atoms in addition to deltahedra of some type. This means that in order to get an optimal electron concentration there have to be either even higher order deltahedra or fused icosahedra. That KB_6 adopts the CaB_6 structure even if it cannot take full advantage of the stability of the octahedron may well be a consequence of the intrinsic preference of boron for low order deltahedra. Contrariwise several gallium phases have N_F values very near 3.33 but nevertheless do not adopt the very simple CaB_6 structure ($N = N_f = 3.33$) but some very complex icosahedral based ones. Both of these observations are an indication of the importance of the somewhat different preferences for boron and gallium.

Acknowledgment. This research was supported by The National Science Foundation under NSF DMR8414175. Much of this work was performed at the Laboratoire de Chimie Thēorique, Universitē de Paris Sud. J.K.B. thanks this laboratory for their hospitality.

Appendix

The calculations were of the extended Hückel type for both molecules[49] and infinite systems.[50] The modified Wolfsberg–Helmholz formula[51] was used. The exponents and parameters are those of Table III. Experimentally based B–B and Ga–Ga distances of 1.72 and 2.70 Å were used in both cases. The deltahedra were regular except when otherwise stated. Experimental distances and angles were used for the Ga_{15} (**15**) and Ga_{10} (**27**) clusters.