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Role of Large but Defective Deltahedra in the Structural Chemistry of Very Complex Solid Borides and Gallides†

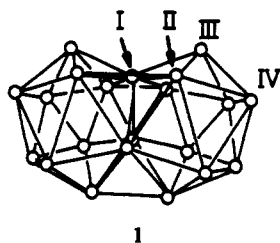
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Large (icosahedra and higher) deltahedra are usually found in extended solid-state arrays with some of their sites not fully occupied, thus giving rise to nonstoichiometric materials. How the electronic characteristics of such deltahedra change with increasing size, the electronic reasons behind the tendency to lose such atoms, and the resulting changes in the electronic structure of the defect deltahedra are described. It is shown that the Wade rule breaks down if two or more adjacent vacancies are created on a deltahedron, and how this influences the electron counting for fused deltahedra is described. Some structural aspects of complex borides and gallides including SiB_6 , AlB_{12} , β -tetragonal boron, $\text{Li}_2\text{Na}_5\text{Ga}_{19.6}$, $\text{Rb}_{0.6}\text{Na}_{6.25}\text{Ga}_{20.02}$, and $\text{K}_3\text{Li}_9\text{Ga}_{28.83}$ are discussed. An interesting correlation is shown between the sign of the computed atom-atom pair potentials and site occupancy for the twinned icosahedron.

Introduction

Recent years have seen the synthesis and structural characterization of several complex borides and gallides, which provide challenges to the experimentalist to accurately pin down their geometric structure and to the chemist who wishes to understand their electronic structure. Many of these systems gave hints that they could be complex materials from their formulas, $\text{Rb}_{0.6}\text{Na}_{6.25}\text{Ga}_{20.02}$ ¹ and $\text{K}_3\text{Li}_9\text{Ga}_{28.83}$ ² for example, but others such as SiB_6 ³ do not. The structures of these materials geometrically are often very complex. Invariably they contain deltahedra linked both to each other directly and via extra atoms in the structure. Sometimes the deltahedra may be geometrically described as arising via the fusion of smaller units. 1 shows the structure of



two face-sharing icosahedra (we will call this entity a twinned icosahedron) found in $\text{Rb}_{0.6}\text{Na}_{6.25}\text{Ga}_{20.02}$ and indicates the nature of another problem. The sites Ga(11) and Ga(29) associated with the atoms of type II are not completely occupied (81% and 51%, respectively) so that nido, arachno, and in principle other even more defective deltahedra are present. Nonstoichiometry is a prominent feature of these systems. From the X-ray diffraction experiment itself, of course, we cannot distinguish between a random ordering of defects in these sites and a structure where the vacancies are correlated on individual icosahedra. Similar units are found in $\text{Li}_3\text{Na}_5\text{Ga}_{19.6}$ ⁴ and $\text{K}_3\text{Li}_9\text{Ga}_{28.83}$.² In $\text{K}_4\text{Na}_{13}\text{Ga}_{49.57}$ ⁵ a triply fused icosahedron is found. The usual rule in most of these systems, including AlB_{10} ,⁶ $\text{C}_8\text{Al}_{2.1}\text{B}_{51}$,⁶ and $\text{C}_4\text{AlB}_{24}$,⁷ is that the icosahedra are defective.

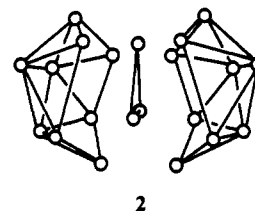
Wade's rules⁸ have long been used to count electrons in systems containing deltahedral clusters, but there are several features that complicate their use in these solids. The first is that the rule which assigns equal numbers of skeletal electrons to closo, nido, and arachno deltahedra of a given size often does not work. As we will see, high-lying orbitals are generated if two vacancies are located adjacent to each other in a deltahedron. The second problem is associated with the extensions of the electron counting rules to deltahedra that are fused to others by edges or faces. As we have described elsewhere,⁹ the rules developed by Mingos¹⁰ and Teo,¹¹ apparently quite successful in transition-metal chem-

istry, do not work in general for these main-group atoms. One of the complications in the main-group case is the close contact between parts of the deltahedra not formally involved in the fusion, but even when these are removed, problems remain as we will see below. Interestingly, we will see that these rules do work for the face fusion of two icosahedra. Yet a third problem concerns the problems involved in packing large deltahedra together. Geometrically it may not be possible to satisfy all of the outward pointing orbitals by making bonds to other deltahedra. Thus, the energetic location of the lone-pair orbitals of the skeletal atoms when no external linkage is present are important to study and may change in energy as the deltahedron becomes larger.

In the materials we describe here these three problems are coupled together to give an electronically complex situation. When linked with their geometric complexity, these systems present quite a challenge. A word of caution is in order too concerning the crystal structures reported for these systems. For almost all of the structures we describe the X-ray data has been refined by using models where some of the sites are only partially occupied by atoms of a particular type. Often the *R* values are not very good. The geometrical structure of the solid is not as well-defined as we would like and thus does not provide the best test-bed for the results of electronic structure calculations.

Fusion of Icosahedra

The electronic structure of a $\text{B}_{21}\text{H}_{18}$ twinned icosahedra (1) can be approached by considering the interaction of two hypoh icosahedra (B_9H_9) with a central B_3 triangle (2). The energy



levels of closo and hypoh icosahedra are reported in Figure 1a,b, respectively. Surprisingly, only 10 of the 13 skeletal orbitals of

- (1) Charbonnel, M.; Belin, C. *J. Solid State Chem.* **1987**, *67*, 210.
- (2) Belin, C. *J. Solid State Chem.* **1983**, *50*, 225.
- (3) Vlasse, M.; Slack, G. A.; Garbaskas, M.; Kasper, J. S.; Viala, J. C. *J. Solid State Chem.* **1986**, *63*, 31.
- (4) Charbonnel, M.; Belin, C. *Nouv. J. Chim.* **1984**, *8*, 595.
- (5) Belin, C.; Charbonnel, M. *J. Solid State Chem.* **1986**, *64*, 57.
- (6) Perrotta, A. J.; Townes, W. D.; Potenza, J. A. *Acta Crystallogr.* **1969**, *B25*, 1223.
- (7) Will, G. *Acta Crystallogr.* **1969**, *B25*, 1219.
- (8) Wade, K. *Chem. Commun.* **1971**, 792; *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.
- (9) Burdett, J. K.; Canadell, E. *J. Am. Chem. Soc.* **1990**, *112*, 7207.
- (10) (a) Mingos, D. M. P. *Chem. Commun.* **1983**, 706. (b) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311. (c) Mingos, D. M. P.; Johnston, R. L. *Struct. Bonding* **1987**, *68*, 31. (d) Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1990.
- (11) (a) Teo, B. K. *Inorg. Chem.* **1984**, *23*, 1251, 1257. (b) Teo, B. K. *Inorg. Chem.* **1985**, *24*, 4209.

† Dedicated to Prof. Hans-Georg von Schnering on the occasion of his sixtieth birthday.

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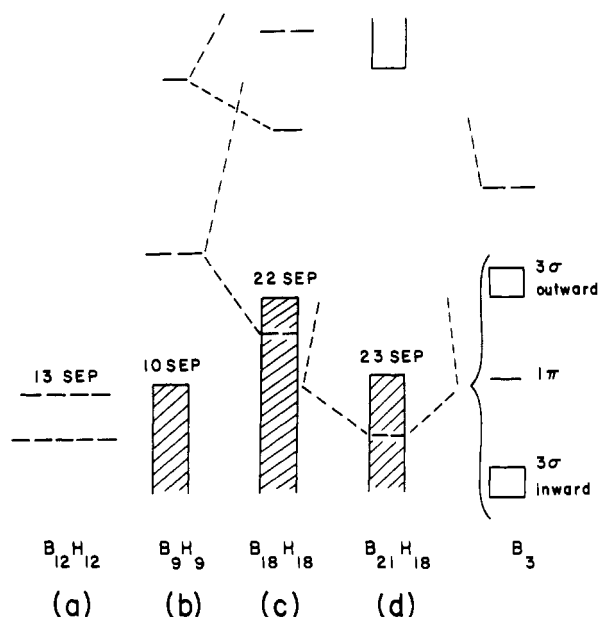
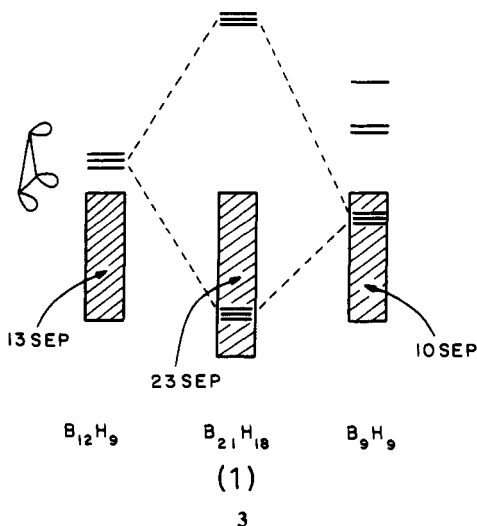


Figure 1. Energy levels for a closely packed icosahedron (a), hypohedron (b), and two hypohedra interacting as in **2** (c) and an interaction diagram for **1** (d).

the closely packed polyhedron remain low lying in the hypohedron. Although the degenerate pair could be lowered by some structural readjustment, the nondegenerate orbital of the set is definitely too high to be filled. In **2**, three quite short contacts are created, and consequently, bonding and antibonding combinations of these three orbitals will be generated. Although the two combinations of the nondegenerate orbital remain very high lying, the bonding combination of the degenerate pair is lowered enough to be filled (Figure 1c). In consequence, the skeletal bonding of these two interacting hypohedra requires 22 electron pairs. We can now insert a B_3 triangle to generate the twinned icosahedron. Seven orbitals of the B_3 unit are bonding (three σ inward pointing and one π) or nonbonding (three σ outward pointing). All of these orbitals find a good match with the skeletal orbitals of the hypohedra, and the associated orbital mixing is quite complex. The result is that a very large energy gap is created for a total of 23 skeletal bonding orbitals (Figure 1d).

The above derivation makes it clear the existence of strong interactions between atoms of type II of the twinned icosahedron, a result that will be important later. A simpler derivation of the required number of skeletal electron pairs is schematically shown in **3**. The relevant levels of an icosahedron with three hydrogen



atoms missing, i.e., 13 skeletal bonding orbitals and 3 "radical" levels, are shown at left. The 10 skeletal bonding levels plus the

Table I. Decrease in the Number of Skeletal Electrons Required for Deltahedral Fusion Using Various Electron Counting Rules for Main-Group Atoms

fusion mode	initial			
	Mingos model {4n - B}	modified Mingos model	Teo model 2 δ	this work
vertex	4	0	4	0
edge	6	4	6	4
face	6	6	6	6

3 high lying ones of the hypohedron are shown at right. The 3 radical orbitals ($a_1 + e$) find a good energy and symmetry match with 3 of the 10 bonding levels of the hypohedron and are very strongly pushed up. Since the symmetry of the three already high-lying orbitals of the hypohedron is $a_1 + e$, they will also be pushed up as a result of this strong interaction. The total number of skeletal bonding levels required for **1** is then $13 + 10 = 23$. A similar approach can be used for vertex- and edge-fused systems.

It is appropriate at this stage to compare our results generated both here and earlier for smaller deltahedra, with the predictions made by the theories of Mingos¹⁰ and of Teo.¹¹ There is unfortunately very little to tie all three approaches together. The Mingos approach states that "The total electron count in a condensed polyhedron is equal to the sum of the electron counts for the parent polyhedra A and B minus the electron count characteristic of the atom, pair of atoms, or face of atoms common to both polyhedra." The electron count characteristic of the atom ($n = 1$), pair of atoms ($n = 2$), or face of atoms ($n = 3$) is simply equal to $\{(EAN)n - B\}$. EAN = 18 for transition-metal and 8 for main-group systems, and B, the number of bonding electrons in the three units, is clearly zero, two, and six for $n = 1-3$. We can rearrange this expression for the skeletal electron count in the condensed polyhedron as equal to the sum of the skeletal electron counts for the two deltahedra less $\{4n - B\}$. The predictions of the Mingos rule, as initially stated, for vertex, edge, and face fusion are given in Table I. In fact, Mingos has recently recognized the problems associated with the general scheme for main-group problems.^{10d} Instead of the use of $(EAN)n - B$, leading to values of 8, 14, and 18, respectively, for vertex, edge, and face fusion, the figures of 4, 12, and 18 are now used. These bring the counting rules (column 3) into agreement with our work (column 5).

Teo's model expresses the electronic requirements in terms of the number of vertices (V) and faces (F) of the polyhedra and a system-dependent parameter (X) as total number of electron pairs = $3V = F + 2 + X$. For deltahedron **1** the number of skeletal pairs is simply $P_1 = 2V_1 - F_1 + 2 + X_1$, since V_1 vertices are used in extradeltahedral bonds. Let us examine the specific case of face fusion of two identical units. In the fused unit the total number of electron pairs is $3V_2 = F_2 + 2 + X_2$. Now $V_2 = 2V_1 - 3$, $F_2 = 2F_1 - 2$, $X_2 = 2X_1$, and there are $2V_1 - 6$ external linkages. The total number of skeletal pairs required is thus $4V_1 - 2F_1 + 1 + 2X_1 = 2P_1 - 3$. In general, the result may be written as $2P_1 - \delta$. Table I shows analogous figures for edge and vertex fusion.

In the third column of Table I are the values that come from our molecular orbital calculations. The figure for vertex fusion comes from a calculation for the fusion of a pair of octahedra where the fusing atom is large enough to preclude interactions between other atoms of the octahedra. The figure for edge fusion comes from the fusion of nido pentagonal bipyramids where such interactions are also absent. The figure for face fusion comes from our study here using icosahedra. Notice that only in this last case do all three approaches agree. The results labeled "this work" are the correct ones (even given the restrictions described earlier) and generate the electron counts that are needed to correctly account for the respectively vertex- and edge-fused structures of $MgCp_2$ ¹² and MgB_4 .⁹ The figure for the twinned icosahedron we shall see is the correct one too.

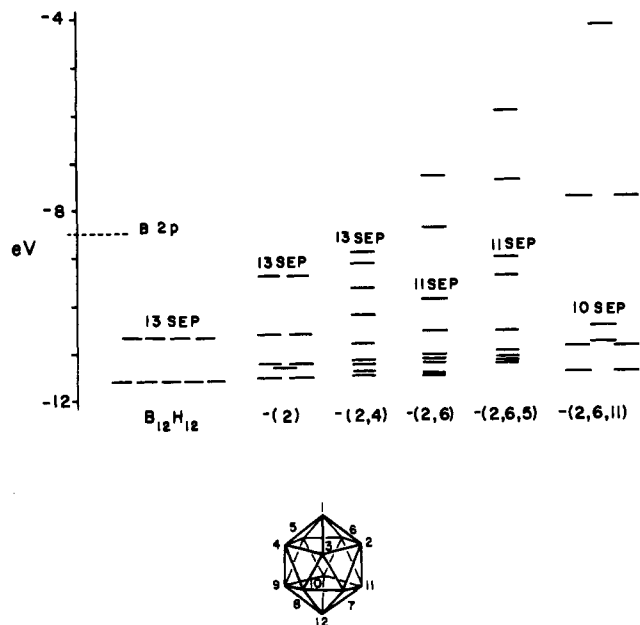


Figure 2. Energy levels for different defect icosahedra. The numbers in parentheses indicate the defective B-H groups.

Table II. Values of N_f for Important Deltahedra

number of vertices	6	8	9	10	12	15
octahedron		dodecahedron	tricapped trigonal prism	bicapped square antiprism	icosahedron	icosihexahedron
closo	3.33	3.25	3.22	3.20	3.17	3.13
nido	3.80	3.57	3.50	3.44	3.36	3.29
arachno	4.50	4.00	3.86	3.75	3.60	3.46

Electronic Structure of Defect Deltahedra

For many molecules and solids containing such clusters the deltahedral unit is not complete. Molecular examples are widespread and include the B_4H_{10} molecule and the isostructural Si_4^{6-} unit in Ba_3Si_4 ,¹³ both of which may be regarded as arachno octahedra. In solids, although the 15-vertex icosihexahedron is found complete in BeB_3 ¹⁴ (as a Be_3B_{12} unit), in SiB_6 , nido, arachno, and hypho units made of Si and B atoms are found.³ Nido icosahedra are found in several systems. Two examples are found in the structures of $Rb_{0.6}Na_{6.25}Ga_{20.02}$ ¹ and $Li_3Na_5Ga_{19.56}$.⁴ We have discovered a rule⁹ that deltahedra or defect deltahedra with more than $N_f = 3.5$ electrons per boron atom (counting electrons using Wade's suggestion that closo, nido, and arachno units are more stable as extended arrays without such deltahedral units. Table II lists the crucial electron counts for some cases of interest. From this rule, the first nido deltahedron that could be stable in a solid is that of the square antiprism. Indeed Sn_9 ⁴⁻¹⁵ and Ge_9 ⁴⁻¹⁶ have this structure and are the first we have been able to find (in a not very extensive literature).

This purely empirical rule may in some cases be supplemented by another consideration. As we have just noted, one of the basic rules of the Wade counting scheme is that an n vertex closo deltahedron requires the same number of skeletal electrons ($n + 1$ pairs) as its nido, arachno, and hypho variants with $(n - 1)$, $(n - 2)$, and $(n - 3)$ vertices, respectively. Although there are exceptions, the rule is quite a good one when used to rationalize the

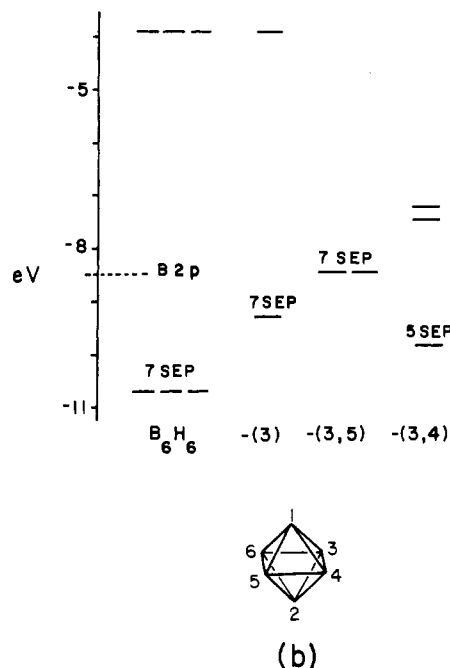
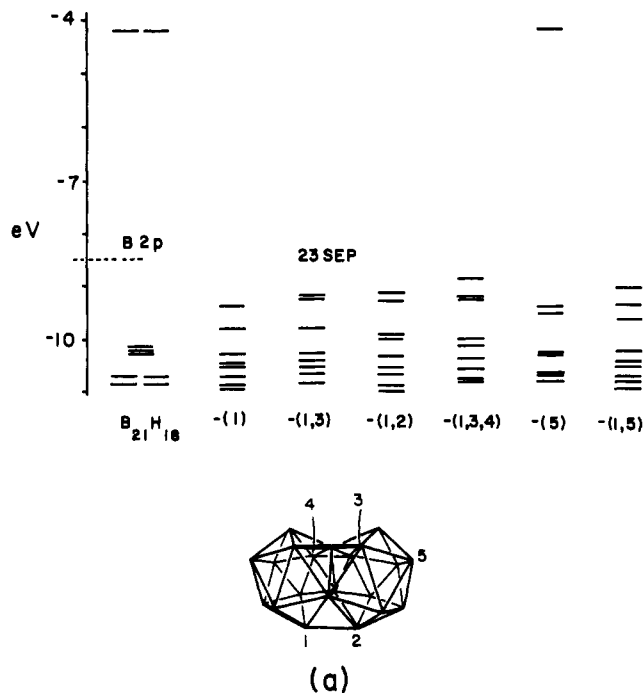


Figure 3. Energy levels for different defect twinned icosahedra (a) and octahedra (b). The numbers in parentheses indicate the defective B-H groups.

structures of molecules. Figures 2 and 3, however, show the energy levels for several defect deltahedra. As noted in the previous section, when the vacancies in the cluster are adjacent to each other, then this rule can break down. There are now orbitals, formally occupied for the $n + 1$ electron-pair count, which lie at an energy higher than that of an isolated boron 2p orbital. Notice that the patterns of these high-lying orbitals mimic the local geometry of the open part of the molecule. Thus, the levels for the icosahedron minus atoms 2, 6, and 11 appear as the two above one pattern expected for the triangle and those for the icosahedron minus atoms 2, 6, and 5 appear as the one above one above one pattern expected for the linear arrangement. In terms of the Stone-Alderton picture¹⁷ of these species, it is not surprising that it is in these cis arachno and hypho species that the rule breaks

(13) Eisenmann, B.; Janzon, K. H.; Schäfer, H.; Weiss, A. *Z. Naturforsch.* **1969**, *24b*, 457.

(14) Mattes, R.; Tebbe, K.-F.; Neidhard, H.; Rethfeld, H. *J. Less-Common Met.* **1976**, *47*, 29.

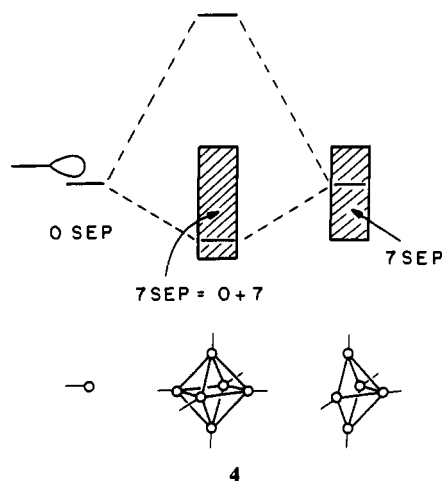
(15) Corbett, J. D.; Edwards, P. A. *J. Am. Chem. Soc.* **1977**, *99*, 3313.

(16) Belin, C.; Corbett, J. D.; Cisar, A. *J. Am. Chem. Soc.* **1977**, *99*, 7163.

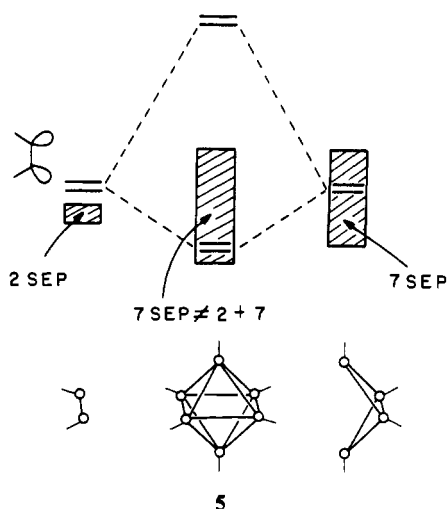
(17) Stone, A. J.; Alderton, M. J. *Inorg. Chem.* **1982**, *21*, 2297.

down, since it is here that the deviation from a spherical geometry is largest.

In fact the existence of these high-lying orbitals is not too surprising and could have been predicted without any calculation. Let us consider an octahedron as resulting from the interaction of a nido octahedron and a B-H group (4). The outward-pointing

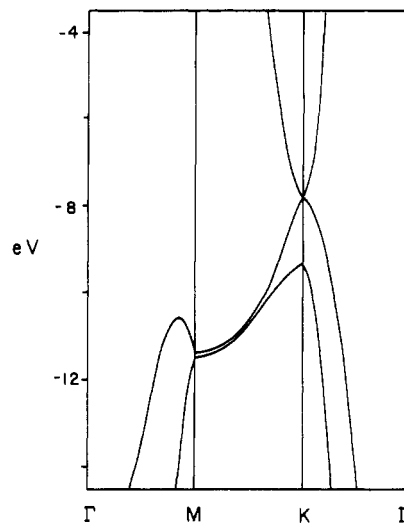


orbital of the B-H group interacts strongly with one of the skeletal orbitals of the nido fragment and is formally pushed up to the antibonding region. The number of skeletal bonding or non-bonding orbitals of the closo and nido octahedra are identical as required by the Wade rules. If we now build the octahedron from an arachno octahedron and a B_2H_2 fragment as shown in 5, the

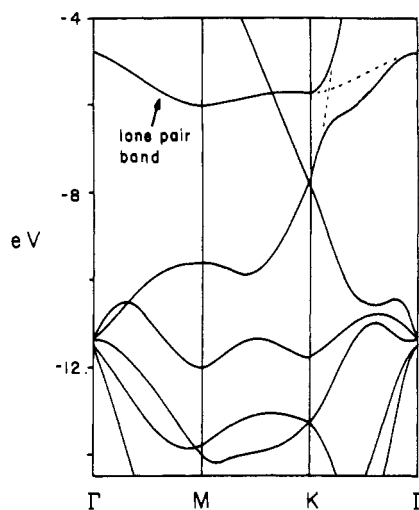


two outward-pointing levels of the B_2H_2 group interact with two of the skeletal orbitals of the arachno fragment and are pushed up in energy. But now since the B_2H_2 group has two skeletal orbitals (one σ and one π), the number of skeletal orbitals of the closo and arachno octahedra should differ by 2. These two extra levels of the arachno octahedron should be a pair of levels lying quite high in energy so that as a result of the main interaction are also destabilized. Note that if the two B-H groups are not adjacent, there is no need for high-lying levels and the skeletal orbitals for the closo and arachno species are identical. Of course the same procedure can be applied to any deltahedron and it is clear that for a hypho icosahedron where the three missing atoms are adjacent there should be three high-lying levels (see Figure 1b). Incidentally, our rules for polyhedral fusion of Table I follow naturally from this approach by replacing the B-H group in 4 by a B_nH_{n-1} deltahedral group, the B_2H_2 group in 5 by a B_nH_{n-2} deltahedral group, etc.

The reason the Wade rules frequently work in molecules of this type is the presence of judiciously located hydrogen atoms that decorate the skeleton or the inclusion of electronegative atoms into the skeleton itself at the sites where the electron density is



(a)



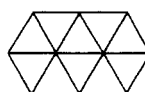
(b)

Figure 4. Band structure for the infinite systems 6 (a) and 7 (b).

concentrated in these high-lying orbitals. For homoatomic, undecorated skeletons of the type frequently found in solids there may then sometimes be a problem in counting. We shall test the importance of this effect later. (Parenthetically we note that the arachno octahedron found in Ba_3Si_4 ¹³ appears to confound both of the considerations described here. It has an N_f value much larger than 3.5, and it has two adjacent vacancies. In fact it is an electron-precise molecule too.)

Lone-Pair Orbitals in Deltahedra

Whereas a tetrahedrally coordinated boron atom requires four electron pairs for electronic stability, it is quite clear that the fourth orbital on a trigonal-planar boron is not filled with electrons. On the other hand, an assumption made in the application of Wade's rules⁸ is that any lone-pair orbitals are indeed filled by a pair of electrons in a cluster. A simple prediction is that as the nuclearity, and hence radius of curvature of the cluster, increases, we expect to reach a particular point where occupation of the lone-pair orbitals might be questionable. The infinite cluster is simply the 3⁶ sheet 6, and a tight-binding band structure calculation on this



6



7

● B-H
○ B

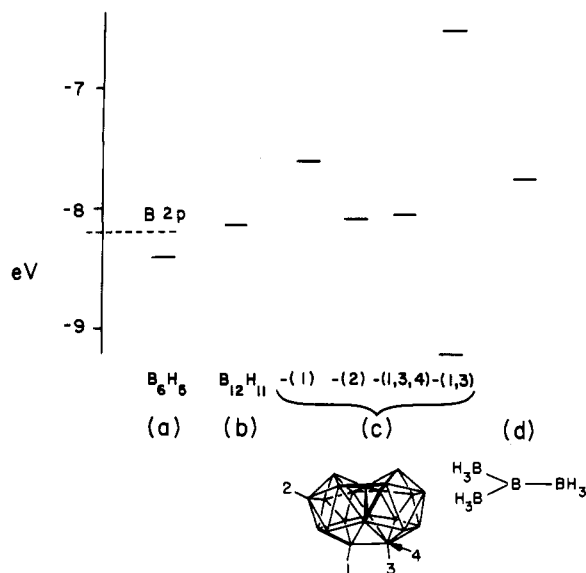


Figure 5. Lone pair energies for octahedral B_6H_6 (a), icosahedral $B_{12}H_{11}$ (b), different units derived from the twinned icosahedra 1 (c), and planar $B(BH_3)_3$ (d). The energy of the 2p boron orbital is also included.

system (Figure 4a) is enlightening.¹⁸ The band structure calculated for the infinite system 7, the appropriate model to estimate the energy of the lone pair in the infinite deltahedra, is shown in Figure 4b. Since the unit cell of 6 contains only one B-H unit, the band structure of Figure 4a contains two filled bands and the Fermi level occurs at K. The unit cell of 7 contains one B and three B-H units. This leads to band folding, which makes Figure 4b apparently more complex. Nevertheless it is easy to see that the band structure of 7 is almost the superposition of the band structure of 6 and a relatively flat band appearing between -5 and -6 eV (notice an avoided crossing along $K \rightarrow \Gamma$). This band is lone pair in character. One of the reasons why, as anticipated, it lies so high in energy is because of the antibonding interactions with the B-H bonding orbitals, which are strong because of the π -type interaction (8).

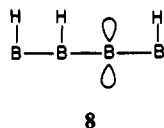


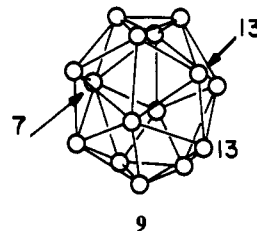
Figure 5 shows the energies calculated for the lone-pair orbitals of a series of deltahedral units B_nH_m (with $m < n$). Notice that the patterns reflect the local geometry. It is interesting to enquire at which critical cluster size might the lone-pair orbital become vacant. (In a heteroatomic cluster of course decreasing the electronegativity of one of the atoms would lead to this result.) Since the structure¹⁶ of Corbett's Ge_9^{4-} species (the highest nuclearity isolated cluster that has been characterized) is predicted by Wade's rules, this point must occur at a larger cluster size. As we will see later, if the lone-pair energy on a cluster is too high, there is a dramatic structural change (loss of an atom) that can occur to lower the energy of the system.

In the following sections we examine the structures of borides and gallides where such large and defective deltahedra are present in order to test out some of these ideas.

Structure of SiB_6

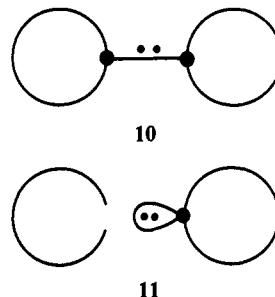
The geometrical structure of this system,³ although appearing complex at first sight, is in fact a relatively simple one in electronic terms. Our discussion will emphasize the special questions to be addressed in those systems where some of the atomic sites are partially occupied by more than one atom. The geometrical arrangement contains icosahedra (A), icosihexahedra (B) (with

15 atoms and 26 faces), isolated atoms (C), and interstitial atoms D. Of the four crystallographically inequivalent icosahedra A, one is composed entirely of boron atoms and the others contain a mixture of boron and silicon. The icosihexahedron is a structural building block found in BeB_3 ¹⁴ too. In this system it is of the stoichiometry Be_3B_{12} and here contains both silicon and boron. Two of the sites are defective (9). Si(7) is occupied 52.6 (5%)



and Si(13) 39.7 (6%) by silicon only. Thus, both closo, nido, and arachno deltahedra are found here (with the same skeletal electron count if we use Wade's rules). Both of the framework atoms C are silicon, but the interstitial atoms D are a mixture of boron and silicon. Neither of these interstitial sites is fully occupied (50.0% and 46.0%, respectively). From the crystal structure determination there are 238.47 boron atoms and 42.65 silicon atoms per unit cell, giving a total valence electron count of 886.01.

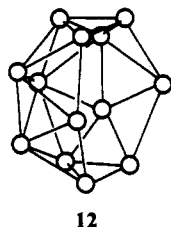
We start by apportioning these in the following (traditional) way. There are 18 icosahedra A each requiring 26 skeletal electrons, and 12 electrons for external bond formation to either the framework atoms or other deltahedra. (This gives a total of 684 electrons.) Each of the four icosihexahedra requires 32 skeletal electrons plus 15 external electrons (a total of 188 electrons). The eight framework atoms C require 4 electrons to form 2c-2e bonds, a total of 32 electrons. The grand total for the framework is 904 electrons. Each atomic site has been counted as if it were fully occupied, since from Wade's rules each nido, arachno, or hypho deltahedron has the same skeletal electron count as the closo parent. In addition, each missing external electron (from a nido, arachno, or hypho deltahedra) has to be counted as half of a lone pair on the atom with which a linkage is made in the closo parent (10, 11). In other words the electron count



required for the skeleton is the same irrespective of the presence of such defects in the structure. There are thus approximately 17 electrons short of the theoretical total.

The discrepancy can be made up by considering the nonstoichiometry of the two icosihexahedral sites in four distinct ways. (a) According to the stated error in the experimentally determined occupancy numbers of the various sites, the error in the number of valence electrons per unit cell is about 3. (b) In addition there is a certain probability that both the labeled atoms (Si(7) or Si(13)) in 9 are defective. In this case the two electrons for the bond should not be counted. Since there are two Si(7)-Si(7) linkages per cell, this leads to a contribution of $4 \times 0.474 \times 0.474 = 0.898$ electrons if the vacancies are statistically ordered or 1.90 electrons if they are correlated. From the X-ray experiment there is no way to decide this. (c) A larger contribution comes from the breakdown of the counting scheme for certain types of arachno and hypho deltahedra, as we have described earlier. The cis arachno icosihexahedron 12 requires only 15 skeletal pairs and not the Wade rule 16 for stability. Results of molecular orbital calculations on several defective $B_{15}H_{15}$ species are shown in Figure

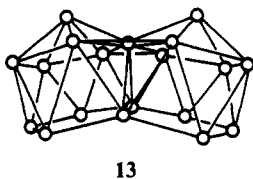
(18) This follows a suggestion made by H. G. von Schnering and R. Nesper.



6. Notice the significant HOMO-LUMO gaps at the relevant positions. If the defects are statistically ordered, the number of electrons not required per cell is 2.9; if correlated, this figure rises to 4.8 electrons per cell. In toto this aspect of the nonstoichiometry can account for about a quarter of the electronic deficit. (d) The largest contribution however, is associated with the possibility that the lone-pair orbitals, lying at a relatively high energy in some of these systems may not be filled. Both Si(7) and Si(13) are only partially occupied, and if the orbitals that point to these vacant sites from other atoms are empty, a smaller number of electrons is required. Si(13) forms linkages to other icosihexahedra, and if these lone-pair orbitals are empty, then $(4 \times 0.474) \times 2 = 3.8$ less are needed. Si(7) forms linkages to icosahedra, and if the lone-pair orbitals on these units are empty, then $(8 \times 0.603 \times 2) = 9.6$ electrons less are needed by the structure. If both sets are vacant, then the total becomes 13.4. The figures associated with the nonstoichiometry are thus quite able to take care of the difference in electron count. The agreement between experimental and theoretical electron counts though is hardly enough to claim that these lone-pair orbitals are definitely empty here.

AlB_{12} and β -Tetragonal Boron

The structure¹⁹ of AlB_{12} is closely related to that of β -tetragonal boron.²⁰ Both contain chains of vertex-linked close icosahedra running in x and y crystallographic directions and twinned icosahedra linked to the atoms of these icosahedra both directly and via framework boron atoms, B(23). The aluminum atoms (in AlB_{12}) sit in interstitial sites in the structure (but different from the interstitial boron sites in β -tetragonal boron). In AlB_{12} two of the sites in the twinned icosahedra are completely vacant (13),



but in tetragonal boron this structural element is complete. In AlB_{12} even though these two sites are strictly "defective", there are no atoms in the rest of the structure that would be linked to them if they were present. Thus, in this case the electron counting should be straightforward. The actual stoichiometry of the material called AlB_{12} is $\text{AlB}_{13.6 \pm 0.2}$, which leads to an electron count per cell of 566.9 ± 7.7 . There are eight icosahedra per unit cell requiring $8 \times 38 = 304$ electrons, four isolated boron atoms needing a total of 16 electrons, and the electrons needed by the four defect twinned icosahedra. As shown earlier, the skeletal electron count for this defective unit is the same (46 electrons) as that for the parent, since the two defects are not adjacent to each other. Along with the 16 electrons needed for the external linkages a total of $4 \times 62 = 248$ is required. Thus, the total electronic requirements per unit cell is 568, a figure in perfect agreement with that found experimentally.

A problem however occurs in β -tetragonal boron.²⁰ This structure is also made up of simple and twinned icosahedra, but unlike the structure of AlB_{12} the twinned icosahedra are complete and not defective. These two new deltahedral atoms (B(24) and

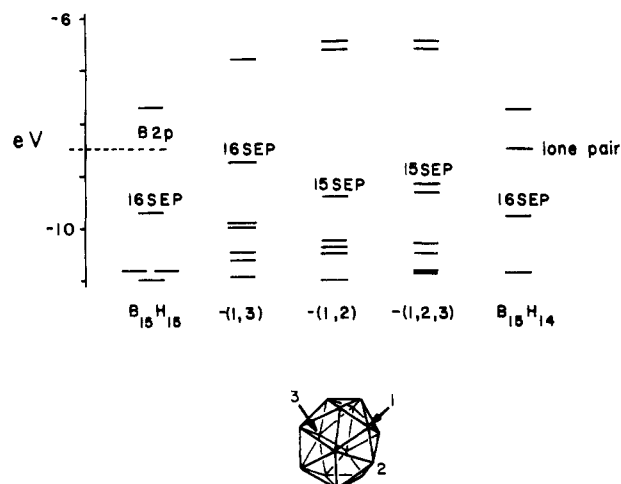


Figure 6. Energy levels for the $\text{B}_{15}\text{H}_{15}$ icosihexahedron and different defect species.

B(24p)) find a sixth, extradeltahedral linkage via new single boron atom spacers. However, there is a real crystallographic problem with these atoms. They sit in sites that are only partially (50%) occupied, have suspiciously short distances to B(23), and look a little like interstitial atoms. The total electron count per unit cell is 561. Let us see what is required for the structure by using the traditional counting method (i.e. 46 skeletal and 18 exo electrons per twinned icosahedron, 26 skeletal and 12 exo electrons per icosahedron, and 4 electrons per tetrahedral boron B(23)). If lone pairs are placed on B(24) and B(24p) and the atoms to which they are attached are treated as interstitial ones, the required figure is 584 electrons for this structure. Without such lone pairs the total electron count required by the structure is 568, close to the figure found from the stoichiometry. Until the crystallographic questions are answered here further progress in understanding the electronic structure of this material unfortunately cannot be made.

Structures of $\text{Li}_3\text{Na}_5\text{Ga}_{19.6}$, $\text{Rb}_{0.6}\text{Na}_{6.25}\text{Ga}_{20.02}$, and $\text{K}_3\text{Li}_9\text{Ga}_{28.83}$

These three systems are quite complex.^{1,2,4} In addition to containing vertex-linked icosahedra, twinned icosahedra are also found. $\text{Li}_3\text{Na}_5\text{Ga}_{19.6}$ and $\text{Rb}_{0.6}\text{Na}_{6.25}\text{Ga}_{20.02}$ are structurally similar and contain deltahedra linked not only directly to each other but also via isolated gallium atoms. Three- and four-coordinate atoms are found in $\text{Li}_3\text{Na}_5\text{Ga}_{19.6}$, but four-coordinated ones, only in $\text{Rb}_{0.6}\text{Na}_{6.25}\text{Ga}_{20.02}$. In all three systems the twinned icosahedra are defective. In $\text{K}_3\text{Li}_9\text{Ga}_{28.83}$ one of these sites is completely empty. Not only are atoms of type II (1) missing in these units but sometimes there is not another gallium atom close to the site from another deltahedron, so that the possibility of lone pairs exists. Charbonnel and Belin¹ have performed an electron-counting exercise for $\text{Li}_3\text{Na}_5\text{Ga}_{19.6}$. There are 2134 valence electrons per unit cell (the stated error via the X-ray determination of the site occupancies is 6 electrons), but they computed a demand for 2163 electrons. This was however assuming a skeletal electron count of 52 electrons for the twinned icosahedron. We have shown above that the correct count is 46. In addition they assumed extradeltahedral two-electron bonds for the waist atoms (type I, 1) of this unit. Whereas the actual number of electrons present in the solid was insufficient for their computed demand of the structure, the reverse is now true (Table III).

In $\text{K}_3\text{Li}_9\text{Ga}_{28.83}$ Belin described² the nido twinned icosahedron as a very defective 11-vertex unit fused to an icosahedron. The twinned icosahedron is nido in the sense that there is one site (capping a pentagonal face) that has an occupancy of zero as described above. Using an estimate of 42 skeletal electrons per nido twinned icosahedron, Belin found a requirement of 808 electrons per unit cell. 788 are present. If a figure of 46 electrons is used and the nonstoichiometry is accounted for, a figure of 793 results. The discrepancies between the numbers of electrons expected on the simplest model and those found experimentally

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Table III. Electron Counting in $\text{Li}_3\text{Na}_5\text{Ga}_{19.6}$, $\text{Rb}_{0.6}\text{Na}_{6.25}\text{Ga}_{20.02}$, and $\text{K}_3\text{Li}_9\text{Ga}_{28.83}$

$\text{Li}_3\text{Na}_5\text{Ga}_{19.6}$		$\text{Rb}_{0.6}\text{Na}_{6.25}\text{Ga}_{20.02}$		$\text{K}_3\text{Li}_9\text{Ga}_{28.83}$	
Skeletal Electrons (A-D are icosahedra, E is a twinned icosahedra)					
4A	104	4A	104	4A	104
8B	208	8B	208	4C	104
16C	416	16C	416		
8D	208	8D	208		
8E	368	8E	368	8B/E ^a	368
Total	1304	1304			578
Outwardly Uncoordinated Deltahedral Atoms Requiring Lone Pairs^b					
On icosahedra					
32 Ga(12)	34	32 Ga(11)	52		
On Twinned icosahedra					
16 Ga(22)	15			8 Ga(13)	12
Total # of Electrons	49	52			12
Isolated Gallium Atoms Requiring Two-Center Two-Electron Bonds^b					
Three-Coordinate					
	96				
Four-Coordinate					
	128		279		
Total # of Electrons	224	279			
Extra-Deltahedral Bonds					
A	46	A	48	A	42
B	87	B	93	C	40
C	176	C	192		
D	96	D	96		
E	106	E	112	B/E ^a	123
Total	513	541			205
Grand Total Required					
	2090	2176			793
Total From Experiment					
	2134	2141			788

^aThis is described in ref 2 as icosahedron B fused to an 11-vertex unit via a face. ^bNonstoichiometry taken into account.

for this collection of closely related species (especially the first two) vary sufficiently that it is unfortunately not possible to say that our more complex model is applicable. The problem, of course, lies with the poorly determined structure.

Defective Deltahedra

So far we have focused on some electronic effects that we expect to see in these large and defective deltahedra. What is interesting to probe are the energetic reasons behind the formation of such species. There are several factors that emerge from our discussion above. As the deltahedra increase in size, it becomes more difficult to pack them together in the solid such that all external linkages are satisfied. Often needed are judiciously placed spacers, usually isolated boron/gallium atoms or small B_n or Ga_n units. If the packing and stoichiometry is such that no spacer is available either, then a lone-pair develops on the cluster. From our calculations the energy of this lone pair becomes less attractive energetically as the cluster size increases and the HOMO of the nido version of this structure (*with the same number of electrons*) lies much lower in energy. Thus, on our one-electron model defective structures are energetically favored. Some supporting evidence for this point of view comes from the structural results described earlier. Very frequently (in, for example, β -tetragonal boron, $\text{Li}_3\text{Na}_5\text{Ga}_{19.6}$, $\text{Rb}_{0.6}\text{Na}_{6.25}\text{Ga}_{20.02}$, and $\text{K}_3\text{Li}_9\text{Ga}_{28.83}$) the boron or gallium atoms that are outwardly uncoordinated only partially occupy their sites. In the structure¹⁹ of AlB_2 where one pair of type II atoms are completely absent there is no spacer present in the structure to outwardly coordinate this site. The other two pairs are not defective and each are coordinated by a spacer atom. From Figure 5 we see that the lone-pair energy at this site lies particularly high in energy. Thus atoms in these positions unless coordinated by extradeltahedral atoms will have a tendency to

Table IV. 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

^aSlater-type orbitals exponents.

be lost.

There are two factors associated with the increase in the radius of curvature that concern the nature of the extradeltahedral B-B linkages themselves. The first is an increase in the repulsion between them. This may be seen at its worst in **8** for the extreme case of the infinite BH sheet where the (nonbonded) H-H distance is the same as the B-B (bonded) one. The second concerns the change in the nature of the outwardly pointing orbitals in the cluster. From consideration of the B-B-B angles these should adopt more p character as the deltahedron becomes smaller with a commensurate increase in the strength of the extradeltahedral B-B linkages as the cluster decreases in size. We have to be careful in using observed B-B distances to support this claim though. The external B-B distance in CaB_6 is 1.67 Å, close to the mean distance between boron atoms on adjacent icosahedra in SiB_6 of 1.69 Å but shorter than the intericosahedral B-B distances in SiB_6 of 1.76 Å. Intericosahedral distances in AlB_{12} , however, average around 1.74 Å. The computed B-H overlap populations for $\text{B}_n\text{H}_n^{2-}$ clusters are similar for $n = 6$ and 12 (0.78 and 0.80, respectively) but smaller than the value (0.94) for the infinite BH sheet. Thus, the increase in steric crowding and the change in hybridization complete in controlling the variation in the strength of an external B-B linkage as the cluster size increases.

A third and special effect is associated with the atoms of type II (1) of the twinned icosahedron, which are forced to be close together by the fusion process. Recall that atoms of this type play an important role in determining the electronic requirements of deltahedral fusion as we discussed earlier.⁹ Although there is a vestigial bond (a bond overlap population of 0.066) calculated between such a pair of boron atoms separated by the fusion plane, the total B-B bond overlap population around this atom is smaller (2.34) than that between type IV atoms for example (2.50). We may however use a recent idea²¹ to quantify this "repulsion", which intuition leads us to expect is important in the defect chemistry of such deltahedra. The concept of the pair potential (ϕ) is not one that has been well used in molecular chemistry, but it simply measures the attraction ($\phi < 0$) or repulsion ($\phi > 0$) between two atoms on a surface, in a solid, or in a molecule. Elsewhere²¹ we describe how it may be computed. We have calculated two pair potentials, one describing the interaction between two type II atoms adjacent to each other across the fused face (and thus geometrically close) and the other between two atoms of the same type but located on the same half of the unit (and thus geometrically separated). In the first case the pair potential is calculated to be very repulsive (1.35 eV) but in the second mildly attractive (-0.32 eV). The presence of such a strong repulsion across the fused part of the structure is one reason that such sites are almost always defective in the solids we have described. Atoms forced to be in such a juxtaposition by fusion are absent in other structures too. In the structure⁹ of MgB_4 only one half of the atoms of the closo pentagonal bipyramid that would be forced to be close to each other are present (leading to a nido pentagonal bipyramid).

The rather special electronic properties of these large deltahedra allow then an explanation of the nonstoichiometry, which is a striking feature of the materials that contain them. In general terms it is not surprising that they can readily accept chemically or electrochemically inserted lithium atoms or that nonstoichiometry is very prevalent. Such considerations also allow insight into the observation that they may be used as negative electrodes in secondary batteries.

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Appendix

The calculations for both molecules and solids were of the extended Hückel type^{22,23} with the exponents and parameters of Table IV. The modified Wolfsberg–Helmholz formula was

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used.²⁴ Except for the icosihexahedron **9**, where the experimental distances found in BeB₃¹⁴ were used, the deltahedra were regular with B–B and Ga–Ga distances of 1.72 and 2.70 Å. The capping atoms used were hydrogen atoms with B–H and Ga–H distances of 1.19 and 1.65 Å. Similar results were found for the electronic structure of these systems independent of whether boron or gallium were used. The same distances were used in the calculations for **6** and **7**. A set of 36 k-points in the irreducible wedge of the hexagonal Brillouin zone were used to calculate the B–B and B–H overlap populations.

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Mechanistic Studies of the Catalytic Reduction of Nitric Oxide by Carbon Monoxide in the Presence of Platinum(II), Copper(I), and Copper(II)

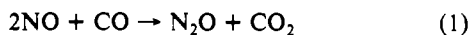
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A rapid reduction of NO by CO to give N₂O and CO₂ is catalyzed at low temperatures and pressures by an aqueous system comprised of K₂PtCl₄, CuCl₂, CuCl, and HCl. Two platinum species, PtCl₃(CO)⁻ and PtCl₄²⁻, were observed and characterized spectroscopically. The former may also be isolated as (AsPh₄)[PtCl₃(CO)] by quenching the reacting catalyst solution with AsPh₄⁺Cl⁻. During the course of catalysis, CuCl absorbs gaseous CO to yield CuCl(CO), which then reacts with PtCl₄²⁻ to give PtCl₃(CO)⁻. No carbonylation of PtCl₄²⁻ and hence no catalysis occur in the absence of CuCl. Isotopic labeling studies by using ¹⁸O-enriched water as the solvent for the catalysis show that the CO₂ evolved contains nearly the same ¹⁸O abundance as in the solvent. In contrast, no ¹⁸O from water is incorporated into the product N₂O. These observations clearly establish that both oxygens in CO₂ are from water and exclude a direct oxygen transfer from NO to CO to yield CO₂. Moreover, the high ¹⁸O content in CO₂ strongly implies the presence of a rapid process of oxygen scrambling between coordinated CO and water. Indeed, PtCl₃(CO)⁻ undergoes oxygen exchange with ¹⁸O-enriched water extremely rapidly without significant decomposition to give CO₂ in the catalyst solution. The reaction of PtCl₃(CO)⁻ with CO to give CO₂ is also too slow to account for the CO₂ production. However, by reaction with NO, PtCl₃(CO)⁻ in the CuCl–CuCl₂–HCl system evolves CO₂ and N₂O rapidly. The presence of CuCl₂ or CuCl in the solution is required for the rapid gas production. This reaction is thought to be the process for N₂O and CO₂ production in the catalysis. Consistent with the observed behavior of the system, the results of kinetic studies may be explained in terms of two kinetically distinguishable processes. One is the carbonylation of PtCl₄²⁻ of which the rate shows first-order dependence on each of [PtCl₄²⁻], P_{CO}, and [CuCl]. The other process is the reaction of PtCl₃(CO)⁻ with NO and water. Its rate is first order on [PtCl₃(CO)⁻], P_{NO}, and [CuCl₂]. For the reaction of PtCl₄²⁻ with CO, the enthalpy of activation is 9.1 ± 0.3 kcal mol⁻¹ and the entropy of activation is -30.2 ± 0.1 cal K⁻¹ mol⁻¹. The corresponding values for the reaction of PtCl₃(CO)⁻ with NO and H₂O are -1.5 ± 0.3 kcal mol⁻¹ and -65.9 ± 0.3 cal K⁻¹ mol⁻¹. On the basis of these two processes, a mechanism for the observed catalysis is proposed.

Introduction

The reduction of nitric oxide by carbon monoxide (eq 1) is a subject of considerable interest, particularly in view of its environmental importance and the extensive bond reorganizations involved. The reaction, while highly exothermic, does not occur



in the absence of a catalyst even at 450 °C.¹ Most studies of the catalysis of reaction 1 used heterogeneous catalysts typically at elevated temperature.² The employment of homogeneous systems for this catalytic reaction has been investigated by several groups. Johnson et al. first reported the reaction of M(NO)₂(PPh₃)₂⁺ (M = Ir, Rh) with CO to give N₂O, CO₂ and M-(CO)₃(PPh₃)₂⁺.³ Subsequently, the catalysis by these dinitrosyl

complexes was explored by Eaymore and Ibers.⁴ Efforts by Eisenberg and his co-workers had led to the discovery of an effective catalyst system consisting of Rh(CO)₂Cl₂⁻, HCl, H₂O, and ethanol for eq 1.⁵ By means of an ¹⁸O isotopic labeling, they showed that one of the oxygen atoms in the CO₂ product is derived from the water in the reaction medium and not directly from the nitric oxide reactant.⁶ In 1978, an aqueous PdCl₂–CuCl₂–HCl system was found to catalyze eq 1 with a rapid rate.⁷ A

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