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New Topological Electron-Counting Theory

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A new topological electron-counting theory based on Euler's theorem and the effective atomic number (EAN) rule is developed to predict electron counts of a large number of polyhedral metal clusters. Each polyhedron (of given numbers of vertices and faces) is characterized by a parameter X, which is defined as the number of "extra" electron pairs "in excess" of the EAN rule. The parameter X for simple, capped, or condensed (via vertex-, edge-, or face-sharing) polyhedra can be estimated from a set of simple, consistent rules. This simple electron-counting scheme can be used to correlate the known structures as well as to predict the yet unknown polyhedra of a wide range of transition-metal or post-transition-metal clusters of varying nuclearity. The results (cf. following paper) are in good agreement with experimental observations as well as other theoretical calculations. Qualitative theoretical justifications for the rules for evaluating the parameter X are also presented.

Introduction

Metal cluster compounds exhibit a wide range of nuclearity with intriguing structural diversity.[1] Systematic efforts aimed at understanding the electronic and stereochemical requirements of these metal clusters have been initiated by several research groups. Particularly noteworthy are the extension of borane-type rules to transition-metal clusters (skeletal electron pair (SEP) theory),[2,3] graph theory,[4] perturbed spherical shell theory,[5] isolobal concept,[2,3,6,7] and the extended Hückel molecular orbital (EHMO),[6-10] Fenske–Hall approximate Hartree–Fock,[11,12] and SCF–$X\alpha$–SW calculations.[13-15]

Although approximate molecular orbital (MO) calculations often provide a better understanding of the electronic structure of a few chosen clusters and the SEP theory has the advantage of simplicity and applicability to many clusters based on or derivable from triangulated polyhedra, transition-metal clusters often exhibit polyhedral frameworks that do not correspond to those of boranes[16] (which are based on or derivable from triangulated polyhedra). Also, metal clusters often exhibit multiple electron counts for the same geometry (with or without structural distortion). Furthermore, with just a few exceptions, e.g. $[Pt_3(CO)_6]_n^{2-}$[17] and $Ni_8(CO)_8(\mu_4\text{-}PPh)_6$,[18] metal cluster compounds seldom show empty cavities greater than octahedral, in contrast to main-group or naked post-transition-metal clusters. These differences suggest that in transition-metal clusters additional atomic orbitals are available for cluster bonding. For metal carbonyl clusters, the occupancy of extra cluster valence molecular orbitals may also be favored by the π-acidity of the carbonyl ligands.

In this paper, a new electron-counting theory that can be applied to a wide range of transition-metal or post-transition-metal clusters is developed. This simple topological electron-counting approach is based on Euler's theorem for polyhedra and the effective atomic number rule for transition-metal complexes. This electron-counting approach, which requires no theoretical calculations, provides new insights into the electronic requirements of various polyhedral cluster structures and their interrelations. We will illustrate the utility of this new electron-counting scheme via a few illustrative examples. Qualitative theoretical justifications of the rules for evaluating the parameter X are also presented. A more extensive application to metal clusters containing 4–20 metal atoms can be found in the following paper.[19]

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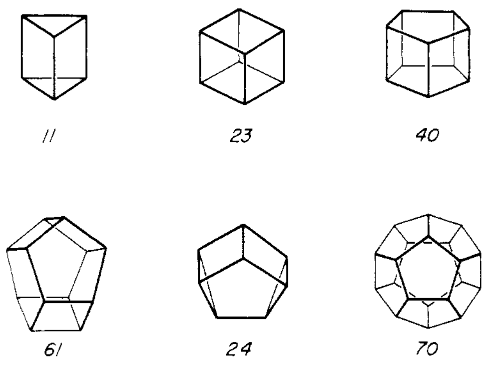
Chart I



3-CONNECTED POLYHEDRA: X = 0
(INCLUDING PRISMS)

Topological Electron-Counting Theory

Consider a *three-dimensional* framework of metal (M) atoms bonded to ligands (L) in a metal cluster. The metal atoms form a *bonding polyhedron* with *regular* faces. Each face consists of three, four, or five metal atoms forming a triangle, a square, or a pentagon, respectively. The edges of each face correspond to a *bonding* metal–metal distance more or less equivalent to that of a single metal–metal bond.

In this paper, we shall restrict our discussions to *spin-paired*, *high-symmetry*, *bonding polyhedra* of V surface metal atoms where $4 \leq V \leq 20$. Ligands, as well as any encapsulated (bulk) metal atoms, are to be considered as electron donors and *not* as part of the polyhedral framework.

For a polyhedron with V vertices, F faces, and E edges, Euler's theorem states that

$$E = V + F - 2 \qquad (1)$$

Assuming each atom on the surface of the polyhedron has the tendency to attain the 18-electron noble-gas configuration (the so-called effective atomic number rule) and that each edge can be considered as a two-center, two-electron metal–metal bond, the total electron count N for the cluster is

$$N = 18V - 2E \qquad (2)$$

The N electrons will fill the $N/2$ energetically low-lying metal *cluster valence molecular orbitals* (CVMO):[8,9]

$$\text{CVMO} = N/2 = 9V - E \qquad (3)$$

When eq 1 is substituted into eq 3

$$\text{CVMO} = N/2 = 8V - F + 2 \qquad (4)$$

However, for a delocalized system not all metal–metal interactions can be considered as two-center, two-electron (2c–2e) bonds. So an adjustment factor X must be added to eq 2–4

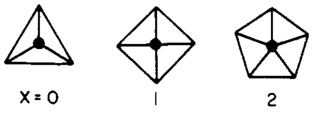
$$\text{CVMO} = N/2 = 9V - E + X \qquad (5a)$$

$$= 8V - F + 2 + X \qquad (5b)$$

where X is the number of "extra" electron pairs "in excess" of the EAN rule. An alternative but equivalent interpretation of X is that it is the number of "false" metal–metal bonds or, in molecular orbital terminology, the number of "missing" antibonding cluster orbitals if each polyhedral edge is considered as a two-center, two-electron bond.

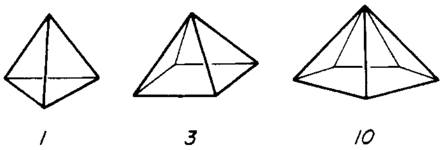
We propose the following simple rules for estimating the value X for a wide variety of polyhedra. Some of the results are tabulated in Table I of the following paper. Throughout this paper, each polyhedron is designated by an *italic* number (cf. first column in Table I of the following paper) for the sake of convenience. We also use the notation ($m^r n^s$...) to denote r m-gonal faces, s n-gonal faces, ..., of a polyhedron. Capping of a trigonal, a tetragonal (or square), and a pentagonal face is represented by the symbols △, □, and ⬠, respectively.

Chart II



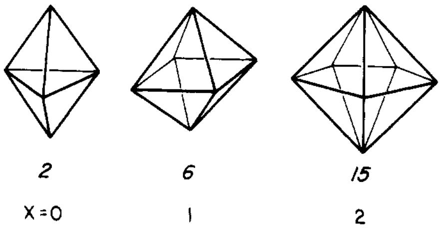
CAPPING : X = (n-3)

Chart III



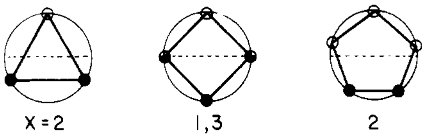
PYRAMIDS: X=0

Chart IV



BIPYRAMIDS VIA CAPPING

Chart V



BIPYRAMIDS : INVERTED HÜCKEL

Rule 1: For all 3-connected polyhedra (i.e. each metal atom is bonded to three other metal atoms), $X = 0$. Examples include all the prisms, cube, ($4^4 5^4$) octahedron, cuneane, ($3^4 6^4$) octahedron, dodecahedron, etc (cf. Chart I).

Rule 2: Capping an n-gonal face of a polyhedron leads to an increase of X by $n - 3$. Hence capping a trigonal, tetragonal (or square), and pentagonal face will give rise to $X = 0$, 1, and 2, respectively (Chart II).

Rule 3: $X = 0$ for all pyramids (Chart III).

Rule 4: The X values for the bipyramids can be determined either by capping the corresponding pyramids as illustrated in Chart IV or by using a graphical rule shown in Chart V. The method of the latter chart resembles that of counting the number of "inverted" Hückel orbitals for the highest symmetry plane of the bipyramid (filled circles). Hence $X = 0$ or 2 for a trigonal bipyramid, $X = 1$, 3 for a tetragonal bipyramid, and $X = 2$ for a pentagonal bipyramid. (The higher values, however, should be considered as "exceptions" because $X = 2$ for a trigonal bipyramid usually means axially elongated (along the 3-fold axis) structures, whereas $X = 3$ for a tetragonal bipyramid is a rare occurrence—only a few examples are known so far—which may also give rise to structural distortion.)

Rule 5: The X values for the antiprisms are determined by a graphical rule illustrated in Chart VI, which can be enlightened to the number of bonding Hückel orbitals (filled circles) for the n-gonal plane. Hence $X = 1$ for a trigonal antiprism, $X = 1$, 3 for a square antiprism, and $X = 3$ for a pentagonal antiprism.

Rule 6: $X = S$ for vertex- or edge-sharing (connected) polyhedra, where S is the number of shared vertices or edges,

Chart VI

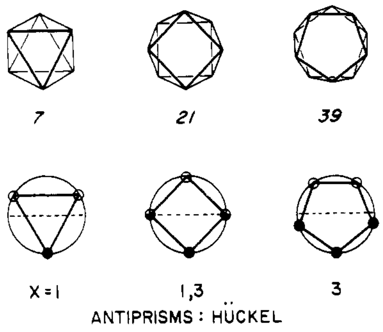
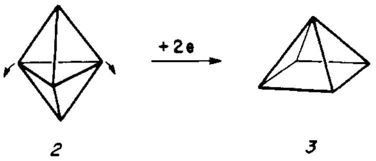


Chart VII



respectively. $X = -H$ for face-sharing (fused) polyhedra (not derivable from simple capping of the components), where H is the number of "hidden" edges.

Rule 7 (structural perturbations of polyhedra): If, by the addition of *Y electron pairs* to a polyhedron with F_1 faces and an X value of X_1, a structural perturbation occurs that converts the original polyhedron to a new polyhedron with F_2 faces, then the X value for the new polyhedron is given by

$$X_2 = X_1 + (F_2 - F_1) + Y \tag{6}$$

The variable Y can be either positive (adding electrons) or negative (subtracting electrons). Equation 6 can be used to estimate the X values for a few polyhedra for which rules 1–6 cannot be applied in a straightforward manner. It should be cautioned, however, that, for large clusters, Y represents the upper limit rather than the precise number of the electron pairs needed to induce the polyhedral transformation (vide infra). The reason is that not all the polyhedral edges can be considered as 2c–2e bonds. This is particularly true if the two polyhedra are quite similar in terms of bonding. We shall discuss this point in a later section.

Qualitative Theoretical Justifications

In this section, we shall provide some qualitative theoretical justification for the phenomenological rules concerning the determination of the value X. A more quantitative account will be published in a forthcoming paper.

Rules 1 and 2 follow directly from the assumption that each metal atom contributes (primarily) three orbitals for polyhedral skeletal bonding. For polyhedral metal clusters in which each metal is bonded to three other metal atoms with two-center electron-paired bonds, we have an "electron-precise" molecule that obeys the EAN rule and hence $X = 0$ (rule 1). As illustrated in Chart II, since each metal atom has only three orbitals available for skeletal bonding, capping a polygon of n atoms means that only 3, not n, metal–metal bonds are being formed. Hence we must add $X = n - 3$ CVMOs to compensate for the $n - 3$ edges subtracted in eq 5a (i.e. the EAN rule overcounts the metal–metal bond pairs by $n - 3$ (rule 2).

The reason that $X = 0$ for the pyramids (rule 3) is illustrated in Charts VII and VIII. A square pyramid (cf. Chart VII) can be formed by adding two electrons to a trigonal bipyramid (with $X = 0$), cleaving one of the equatorial edges. In this process, the number of faces decreases by 1 (from 6 to 5), which precisely accounts for the increase of the number of electron pairs by 1 (cf. eq 5b and 6). In other words, a square structure can "store" two electrons more than two triangles sharing an edge can. Similarly, a pentagonal pyramid (Chart VIII) can be formed by breaking the basal edge closest to the capping atom of a capped square pyramid via addition of two electrons. Again the number of faces decreases by 1 (from 7 to 6), which exactly accounts for the increase by 1 of the number of bonding skeletal electron pairs. Hence $X = 0$ remains unchanged.

Chart VIII

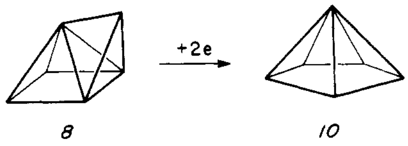


Chart IX

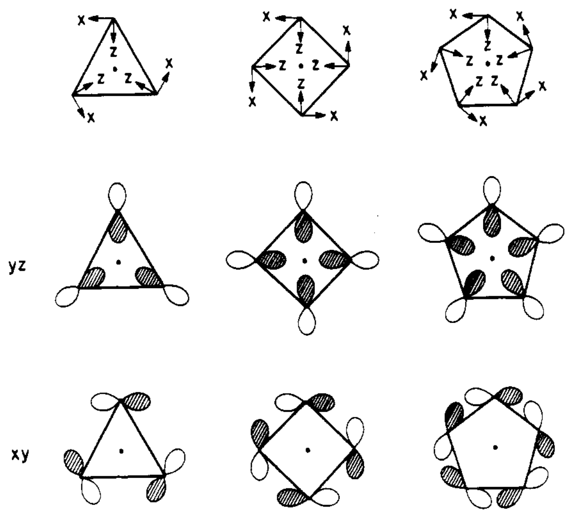
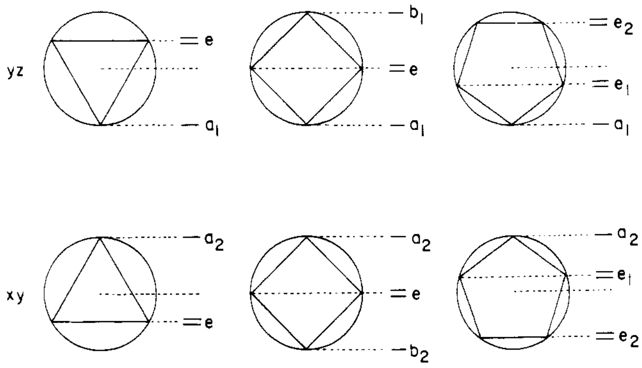


Chart X



The X values for bipyramids (rule 4) and antiprisms (rule 5) can be deduced in the following way. Consider the equatorial plane of the bipyramids. Each equatorial atom needs two out-of-plane orbitals to interact with the two apical atoms. These two orbitals can be hybridized to give an "inward" orbital (yz) and a "tangential" orbital (xy) as illustrated in Chart IX (only $a_1(yz)$ and $a_2(xy)$ orbitals are shown in each case). Symmetrization of the "inward" orbitals gives rise to the Hückel type group orbital diagram (yz) and a similar treatment of the "tangential" orbitals gives the "inverted" Hückel type group orbitals (xy) as shown in Chart X. Since the "inward" orbitals point directly at the apical atoms in the bipyramids, their interactions with the apical atoms are much stronger than those of the "tangential" orbitals. Hence, the resulting bonding molecular orbitals of the former interactions (yz) will lie at lower energies and be filled first. The relative ordering of the corresponding antibonding orbitals will be just the opposite. The "excess" skeletal electron pairs therefore preferentially occupy the tangential xy orbitals for bipyramids. The number, X, can be estimated by the number of low-lying tangential *xy* group orbitals which are bonding or nonbonding between the "in-plane" atoms: viz., $X = 2$ (e) for a trigonal bipyramid, $X = 1$ (b_2) or 3 (b_2 + e) for a square bipyramid or octahedron, and $X = 2$ (e_2) for a pentagonal bipyramid (cf. bottom half of Chart X) under C_{nv} symmetry. The above treatment also predicts that $X = 2$ should have an elongated structure with the axial–equatorial distances being substantially longer than the equatorial–equatorial distances since the e(*xy*) orbitals being occupied are antibonding between the "in-plane" and the "out-of-plane" atoms (but bonding between the "in-plane" atoms). This is indeed observed (vide infra).

The situation for antiprisms is opposite to that of bipyramids. Here the "tangential" orbitals point toward the atoms of the other layer and hence interact more strongly with them than the "inward" orbitals (cf. Charts IX and X). Thus, the bonding (with respect to interlayer interaction) "tangential" *xy* orbitals will be filled first and the "excess" skeletal electron pairs, if any, will occupy the "inward" *yz* orbitals. The number, *X*, can again be estimated by the energetically low-lying *yz* group orbitals which are either bonding or nonbonding among the "in-plane" atoms—viz., $X = 1$ (a_1) for a trigonal antiprism or octahedron, $X = 1$ (a_1) or 3 (a_1 + e) for a square antiprism, and $X = 3$ ($a_1 + e_1$) for a pentagonal antiprism.

Vertex-sharing or edge-sharing (connected) polyhedra (rule 6) follow the modified Euler's equation

$$E = V + F - 2 - S \qquad (7)$$

where *S* is the number of shared vertices or edges, respectively. From eq 5, $X = S$. Face-sharing or fused polyhedra follow the modified Euler's equation

$$E = V + F - 2 + H \qquad (8)$$

where *H* is the number of "hidden" edges (buried inside the fused polyhedron). From eq 5, $X = -H$. If no hidden edges are present or the hidden edges are lengthened to a nonbonding distance, then $X = 0$. Note also that *only the exposed faces are included in the face count F.*

Finally, rule 7 follows directly from eq 5b since the number of vertices remains unchanged.

We close this section by noting that the *X* values predicted by the various rules for the same or similar polyhedra are quite consistent. For example, an octahedron can be considered as a capped square pyramid, a trigonal antiprism, or a square (or tetragonal) bipyramid with 12 equal edges. The predicted *X* values are 1, 1, 1, and 3, respectively. In fact, the majority of octahedral metal clusters conform to $X = 1$.

The equivalent interpretation of *X* as (1) the number of electron pairs "in excess" of the EAN rule or (2) the number of "false" metal–metal bonds (or, in the molecular orbital language, the number of "missing" antibonding cluster orbitals) can be illustrated with tetrahedral and octahedral clusters. In a tetrahedral cluster all six edges can be considered as two-center, two-electron bonds. The EAN rule works and $X = 0$. In an octahedral cluster the value of *X* is 1, which means that there is one electron pair "in excess" of the EAN rule. In molecular orbital terminology, there are 11 rather than 12 antibonding cluster orbitals and hence we have the equivalent of 11 rather than 12 metal–metal bonds, which means that there is one "false" metal–metal bond (note that an octahedron has 12 edges). In this respect, the electron counting scheme described in this paper may also be termed as *topological electron-orbital* counting theory.

Results and Discussion

The topological electron-counting theory proposed in this paper applies only to *bonding polyhedral* metal clusters with more or less compact structures. The polyhedra are formed by regular polygons with edges corresponding to *single metal–metal bond* distances. Each metal atom more or less satisfies the effective atomic number (or the 18-electron) rule. If any of these criteria are relaxed, "exceptions" to these rules can occur. Extension of the topological electron-counting theory presented here to the "exceptions" will be described elsewhere.

The simple electron-counting scheme developed in this paper can be used to predict the number of electrons required for a wide range of transition-metal cluster or post-transition-metal naked clusters. Some of these results are tabulated in Table I of the following paper.[19] Also included in Table I (following paper) are the observed electron counts along with some illustrative examples. (Note that in this and the following paper, each polyhedron is designated by an *italic* number for the sake of convenience). While Table I (cf. following paper) is self-explanatory, a few representative examples will be discussed here to illustrate the utility of the theory.

Counting Electrons. The *total electron count*, *N*, of a given cluster is determined in the usual way by adding up the valence electrons contributed by the metal atoms and the electrons donated to the metals by the ligands. Thus, a rhodium atom has nine valence electrons, a carbonyl ligand (terminal or doubly or triply bridging) is a two-electron donor, a nitride is a five-electron donor, etc. Special attention should be paid to the difference between *surface* and *bulk* ligands. For example, $N = (8 \times 9) + (2 \times 4) + (4 \times 4) + (8 \times 3) = 120$e for the cuneane-like cluster $Co_8S_2(N\text{-}t\text{-}Bu)_4(NO)_8$[20] and $N = (10 \times 9) + (1 \times 6) + (22 \times 2) + 2 = 142$e for the bicapped-square-antiprismatic cluster $[Rh_{10}S(CO)_{22}]^{2-}$.[21] In the former case, each "surface" sulfur (with one lone pair) donates four electrons whereas, in the latter case, the encapsulated "bulk" sulfur contributes all six of its valence electrons to the cluster.

Rules for the Determination of *X*. The following examples illustrate how each of the rules for the determination of parameter *X* can be applied to a given polyhedron.

First, the 3-connected polyhedra (cf. Chart I), including the prisms, have $X = 0$ (rule 1). With five faces, the trigonal prism *11* is predicted to have 90 electrons (as is observed in, for example $[Rh_6C(CO)_{15}]^{2-}$[22] and $[Co_6N(CO)_{15}]^{-}$[23]); with six faces, the cube *23* is predicted to have 120 electrons (as observed in $Ni_8(PPh)_6(CO)_8$[18]), and with seven faces, the pentagonal prism *40* is expected to have 150 electrons (yet unknown). The cuneane-type cluster *24* ($V = 8$, $F = 6$, $X = 0$), a 120-electron cluster (cf. Chart I and eq 5b) was observed in $Co_8S_2(N\text{-}t\text{-}Bu)_4(NO)_8$.[20] A tetrahedron can be considered as either a 3-connected polyhedron or a pyramid; both rule 1 and rule 3 give $X = 0$. Equation 5b predicts an electron count of 60e ($V = 4$, $F = 4$) as is indeed observed in, e.g., $(\eta^5\text{-}C_5H_5)_4Fe_4(CO)_4$,[24] $Fe_4(NO)_4S_4$,[25] and $Ir_4(CO)_{12}$[26a] or $Co_4(CO)_{12}$.[26b]

Second, capping one of the triangular faces of a square pyramid gives capped square pyramid *8* (cf. Chart VIII); rule 2 predicts $X = 0$. With six vertices and seven exposed faces, eq 5b predicts an electron count of 86e as is indeed observed in $Os_6H_2(CO)_{18}$.[27] In contrast, capping the square face of the square pyramid gives the octahedron which has $X = 1$ (rule

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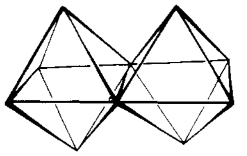
Chart XI



37

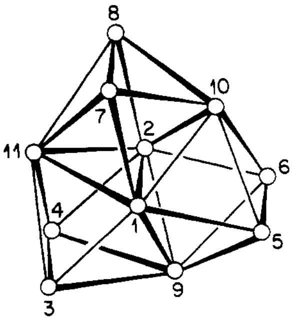
2). With $V = 6$ and $F = 8$, $N = 86$e is predicted as is observed for the majority of octahedral metal clusters.[28,29]

Third, rule 3 applies to all pyramids, resulting in $X = 0$ (cf. Chart III). Hence, tetrahedron *1*, square pyramid *3*, and pentagonal pyramid *10* are predicted to have 60, 74, and 88 electrons, respectively. Most of the tetrahedral clusters have 60 electrons.[24-26] One example of the 74e square-pyramidal cluster is $Ru_5C(CO)_{15}$.[30] No examples are yet available for pentagonal-pyramidal metal clusters.

Fourth, the X values for the bipyramids can be determined by either capping the corresponding pyramids as illustrated in Chart IV or by using a graphical rule shown in Chart V. The latter scheme resembles that of counting the number of "inverted" Hückel orbitals for the highest symmetry plane of the bipyramid (filled circles). Hence $X = 0$ or 2 for a trigonal bipyramid, $X = 1, 3$ for a tetragonal bipyramid, and $X = 2$ for a pentagonal bipyramid. (The higher values, however, should be considered as "exceptions" in that $X = 2$ for a trigonal bipyramid usually means axially elongated (along the 3-fold axis) structures whereas $X = 3$ for a tetragonal bipyramid is a rare occurrence (only a few examples are known so far), which may also give rise to structural distortion.) Equation 5b therefore predicts electron counts of 72e and 76e for trigonal-bipyramidal, 86e (or 90e) for octahedral (or tetragonal-bipyramidal), and 100e for pentagonal-bipyramidal metal clusters. The obvious examples are as follows: (a) trigonal pyramidal structures, 72e, $Os_5(CO)_{16}$,[31] Sn_5^{2-}, Pb_5^{2-};[32] 76e, $[Ni_5(CO)_{12}]^{2-}$,[33] $[Rh_5(CO)_{14}I]^{2-}$;[34] (b) octahedral structures, 86e, $Rh_6(CO)_{16}$,[28] $[Fe_6C(CO)_{16}]^{2-}$;[29] 90e, $Ni_6(\eta^5\text{-}C_5H_5)_6$,[35] $Fe_6S_8(PEt_3)_6^{2+}$.[36] The pentagonal-bipyramidal structure is yet unknown in metal cluster chemistry.

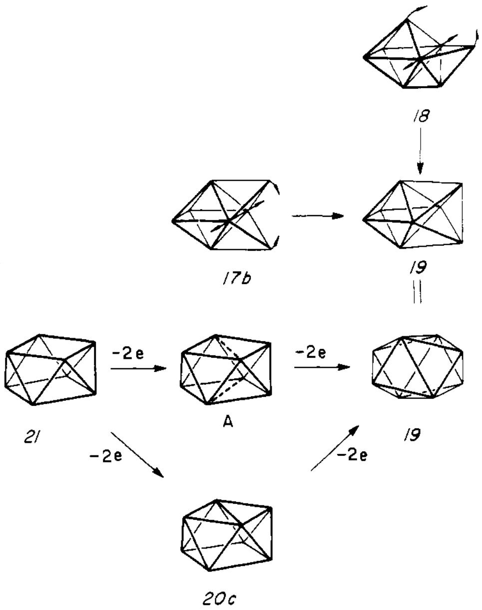
Fifth, rule 5 (cf. Chart VI) gives $X = 1$ for a trigonal antiprism, $X = 1, 3$ for a square antiprism, and $X = 3$ for a pentagonal antiprism. The predicted electron counts are as follows: 86e for trigonal-antiprismatic metal clusters (as is observed in $[Ni_6(CO)_{12}]^{2-}$[37]); 114e and 118e for square-antiprismatic metal clusters (e.g., 114e was observed in $[Co_8C(CO)_{18}]^{2-}$[38] and 118e was observed in $[Ni_8C(CO)_{16}]^{2-}$[39]). Pentagonal-antiprismatic structures have not been observed in metal cluster chemistry.

Chart XII



41a

Chart XIII



Sixth, to illustrate the utility of rule 6, let us consider the edge-sharing bioctahedron shown in Chart XI. A total X value of 3 is expected for this structure since each octahedron contributes an X value of 1 (rule 4) and edge-sharing (rule 6) further increases the X value by 1. With 10 vertices and 16 exposed faces, the electron count is predicted to be 138e. The observed electron count in $[Ru_{10}C_2(CO)_{24}]^{2-}$ dianion,[40] which has two carbides, one in each of the two octahedral holes, is $(10 \times 8) + (2 \times 4) + (24 \times 2) + 2 = 138$e. As an example of a hidden edge, Chart XII depicts the metal framework of the $[Ru_{11}(CO)_{23}]^{3-}$ trianion,[41] whose structure can be described as a face-to-face fused trioctahedron (*41a*). The net X value is 2 for this cluster since three octahedra give rise to a total X value of 3 (rule 4) and one "hidden edge" *within* the polyhedron contributes an X value of -1 (rule 6). With 18 "exposed" faces eq 5b predicts an electron count of 148e, as is indeed observed. If the "hidden" edge is lengthened by adding two electrons to *41a*, the yet-unknown polyhedron of face-to-face trioctahedra without the central edge (*41b*) and with 150-electron count is expected.

Finally, the utility of rule 7 is best illustrated by Chart XIII, which shows how the X value of a triangular dodecahedron can be determined via polyhedral structural perturbation. As shown in Chart XIII, the eight-vertex triangular dodecahedron or dodecadeltahedron (*19*) can be formed by closing one nonbonding edge while opening another of a bicapped octahedron (*17b*) or a fused octahedron and trigonal bipyramid (*18*); the numbers of edges or faces remained unchanged in

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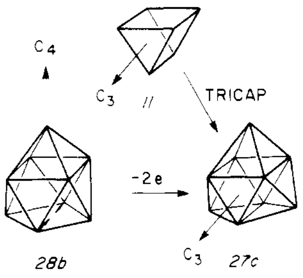
Chart XIV



both cases and hence $X = 1$. Another route to *19* is to remove two electron pairs ($Y = -2$), one from each of the two square faces of a square antiprism *21*, thereby forming two new metal–metal bonding interactions (Chart XIII) and hence shortening the two metal–metal distances involved either via structure A or structure *20c*. In the process, the two square faces are buckled to form triangle faces ($F_2 - F_1 = 4-2 = 2$), and from eq 6, $X_2 = X_1 = 1$ or 3 remains unchanged. With 8 vertices and 12 faces, a triangular dodecahedral metal cluster is predicted to have 110 or 114 electrons. No known structures are yet available.

Capping. As is evident from Table I of the following paper, though capping the different faces of a polyhedron may give rise to different X values, the resulting electron count remains unchanged. For example, capping the triangular vs. the square face of a trigonal prism gives rise to $X = 0$ and 1, respectively, yet both are 102e systems. The reason is that though capping a n-gonal face causes an increase in X by $n - 3$, the total number of faces increases by the same quantity and hence N remains unchanged (cf. eq 5b). This observation is analogous to Mingos' capping principle[42] that the number of polyedral skeletal MOs are unchanged by capping.

Multiple X Values. As the number of vertices increase, the number of possible polyhedra increases rapidly and the electron count becomes increasingly difficult to predict due to the fact that the cluster valence molecular orbitals become increasingly closer to one another such that a cluster may take on several values of electron count and remains more or less stable. For the same reason, a cluster may take on several X values depending on how the polyhedron is derived, described, or approximated. In some cases the metal polyhedral structure remains unaffected whereas in other cases the polyhedron may be perturbed for different electron counts. The latter case is exemplified by the two electron counts for a trigonal bipyramid: a 72e ($X = 0$) system[31,32] has all nine metal–metal distances more or less equal whereas a 76e ($X = 2$) system[33,34] often has a trigonally elongated structure with the apical–equatorial metal–metal distances being significantly longer than the corresponding equatorial–equatorial distances. An even more interesting example is the tricapped trigonal prism. For the nine-vertex tricapped ($\square^3$) trigonal prism *27c*, rule 2 predicts $X = 3$ for capping the three square faces of a trigonal prism *11* (Chart XIV). A second route to a tricapped trigonal prism (a deltahedron) is to remove one electron pair ($Y = -1$) from the square face of a monocapped ($\square$) square antiprism (*28b*), thereby forming a new metal–metal bond and buckling the square face to form two triangle faces ($F_2 - F_1 = 1$). Again $X_2 = X_1 = 2$ or 4 remains unchanged (cf. eq 6). Thus the expected X value for a tricapped trigonal prism is 2, 3, or 4. Equation 5b gives electron counts of 124, 126, or 128 electrons, respectively. Since the 126-electron count is derived from $X = 3$ via tricapping a trigonal prism of D_{3h} symmetry and the 124- or 128-electron count is derived from $X = 2$ or 4 via perturbation of a square-face-capped square antiprism of D_{4v} symmetry, it is conceivable that a 126e tricapped trigonal prism will conform more to the D_{3h} symmetry than a 124- or 128-electron system which may have a structure approaching that of a distorted monocapped square antiprism (rhombic distortion of the square face). The Ge_9^{2-} dianion[43] is an example of a 128e tricapped trigonal prism that is distorted away from D_{3h} symmetry along the C_{2v} pathway toward the C_{4v} symmetry of a capped square antiprism (see ref 43). We take this observation as good evidence that *multiple X values can mean perturbation in the polyhedral structure and/or variation in the cluster bonding capabilities (requirements)*.

Chart XV

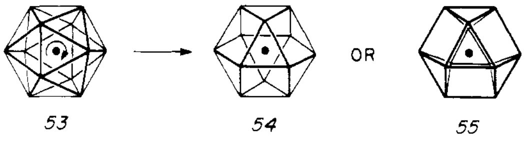
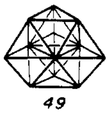


Chart XVI



Polyhedral Transformation. It should be emphasized that, for clusters of high nuclearity, small structural perturbations, which amount to relatively small energy changes, can transform the cluster from one polyhedron to another. Some examples have been shown in Charts XIII and XIV. Yet another example is the transformation of icosahedron to cuboctahedron or twinned cuboctahedron. As shown schematically in Chart XV, the cuboctahedron *54* can be visualized as formed by adding Y electron pairs to an icosahedron *53*, thereby resulting in a lengthening of six metal–metal distances. Since 12 triangular faces are converted to 6 square faces ($F_2 - F_1 = -6$), the X value for a cuboctahedron becomes $7 - 6 + Y = 1 + Y$ (note that 7 is the X value for the icosahedron). Since each edge of an icosahedron probably corresponds to a metal–metal bond order of less than unity, we expect Y to be $1 \leq Y < 6$. The same X value applies to the twinned cuboctahedron *55*, which is related to the cuboctahedron by rotating one of the two triangles about the principal symmetry axis by 60° (cf. Chart XV). With $V = 12$, $F = 20$, and $X = 7$ (bicapping a pentagonal antiprism: $X = 2 \times 2 + 3$), an icosahedral metal cluster is predicted to have 170 electrons, as is indeed observed in the $[Rh_{12}Sb(CO)_{27}]^{3-}$ trianion.[44] A twinned cuboctahedron was observed for the 170e systems $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ corresponding to $Y = 0$ and $X = 1$.[45] Similar values are expected for a cuboctahedron, which is yet unknown in metal cluster chemistry. The reason that the conversion of an icosahedron to a cuboctahedron or a twinned cuboctahedron requires a Y value of 0 rather than 6 is that, for these three polyhedra, despite their distinctive symmetries, the bonding requirements are quite similar. Hence, for large clusters, Y represents the upper limit rather than the precise number of electron pairs required to induce the polyhedral transformation. Note also that the cuboctahedron (*54*) has an A, B, C pattern, corresponding to cubic close-packed (ccp), whereas the twinned cuboctahedron (*55*) has an A, B, A pattern, corresponding to the hexagonal close-packed (hcp) structure shown in Chart XV.

Finally, it is also obvious from eq 6 (rule 7) that if the addition of Y electron pairs results in a loss of Y faces ($F_2 -$

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(42) See ref 23 in ref 10b of this paper.

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$F_1 = -Y$) of a given polyhedron, the X value remains unchanged. Examples have been shown in Charts VII and VIII.

Polyhedral Holes and Condensed Polyhedra. It is possible to invoke the concept of "polyhedral holes" in place of face-sharing "fused (or condensed) polyhedra". Rule 6 applies to both concepts.[46] One example is the truncated ν_2 (frequency two, meaning that each edge corresponds to two metal–metal bonds) trigonal bipyramid (*49*), shown in Chart XVI, which has two octahedral holes and three trigonal-bipyramidal holes. If each octahedral hole contributes $X = 1$ (rule 4) and each trigonal-bipyramidal hole contributes $X = 2$ (rule 4), with three "hidden edges" (inner triangle of the center layer), $X = -3$ (rule 7), a net X value of 5 can be calculated. The predicted electron count is thus 166e as is indeed observed in the $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ anions.[47] We note that the interlayer metal–metal distances are longer than the intralayer metal–metal bonds, in accord with the use of the X value of 2 for each of the three trigonal-bipyramidal holes. We predict that an electron count of 160e is more appropriate for a similar structure with more or less equal inter- and intralayer metal–metal distances.

Cage Size. It is evident from eq 5b that for a given number of vertices (V), as the number of faces (F) decreases, the cage size increases and hence the number of electrons (N) that can be "stored" in the cage increases. The cage may reach a size big enough to completely "encapsulate" a metal atom of approximately the same size for 12-vertex polyhedra or above. Notable examples include the icosahedron, cuboctahedron or twinned cuboctahedron, bicapped pentagonal prism, etc. Besides, the cage size must be more or less spherical (and of the right dimension) to completely incorporate atoms such as carbide, nitride, sulfide, or metal atoms. Two examples of the nonspherical cage are those within the dodecadeltahedron (which is ellipsoidal) and within the pentagonal bipyramid (which is disklike).

Conclusion

In summary, we have developed in this paper a new topological electron-counting theory based on Euler's theorem and the effective atomic number rule. Each polyhedron (of given numbers of vertices and faces), be it simple, capped, or condensed (via vertex, edge, or face sharing), is characterized by a parameter X, which can be determined from a set of simple rules. This simple scheme can also be used to predict the electron counts as well as to correlate the structures of a wide range of metal clusters of varying nuclearity (cf. following paper), thereby enabling one to achieve a better understanding of the interrelationships between the various cluster geometries.

Acknowledgment. I am indebted to Drs. N. J. A. Sloane and F. R. K. Chung of Bell Laboratories (Murray Hill, NJ) for many useful discussions concerning properties of polyhedra and to Kelly Keating (Bell Labs) for helpful comments. I am also grateful to Prof. J. Lauher for suggesting the alternative interpretation of X (as the number of "false" metal–metal bonds), to Prof. D. M. P. Mingos for many helpful suggestions concerning the manuscript, and to Drs. G. Longoni, S. Martinengo, A. Ceriotti, A. Fumagalli, L. Garlaschelli, M. C. Malatesta, D. Strumolo, and A. Albinati for numerous stimulating discussions during my 1-month visit at the Instituto di Chimica Generale dell'Università, Milan, Italy, in 1982.

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Applications of Topological Electron-Counting Theory to Polyhedral Metal Clusters[1]

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The simple topological electron-counting theory developed in the previous paper is applied to a wide range of transition-metal and post-transition-metal clusters of varying nuclearity. The results are in excellent agreement with experimental observations. This simple electron-counting scheme provides an alternative to the skeletal electron pair theory in that it can be used to correlate the known as well as to predict the yet unknown polyhedral structures of a general nature. The theory also provides a better understanding of the interrelationships between different cluster geometries.

Introduction

The last decade or two has witnessed a dramatic increase in interest in metal cluster chemistry. Principles underlying the stereochemistry and bonding of metal cluster compounds are generally well established through synthetic, structural, spectroscopic, and theoretical studies.[2] On the one hand, simple electron-counting schemes such as the effective atomic number (EAN) and the skeletal electron pair (SEP)[3,4] rules, which result from these systematic studies, are extremely useful in correlating the structures of a vast number of clusters to their electron counts. On the other hand, more insight can be gained through more elaborate treatments such as graph theory,[5] perturbed spherical shell theory,[6] isolobal concept,[3,4,7,8] and the extended Hückel molecular orbital (EHMO),[7-11] Fenske–Hall approximate Hartree–Fock,[12,13] and SCF–Xα–SW calculations[14-16] (in the order of increasing calculational complexity).

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