Translated from *Uspekhi Khimii*, 54, 556-590 (1985) U.D.C. 541.57

The Structure of Cluster Compounds of Transition Metals and the Limits of Applicability of the Electron Counting Rules for Polyhedral Molecules

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The current theoretical ideas concerning the electronic structure of clusters and electron counting schemes for them derivable from molecular orbital analysis, whereby one can determine magic numbers of valence and skeletal electrons corresponding to energetically favourable characteristic geometrical configurations of cluster polyhedra, are examined. Among the multiplicity of polynuclear compounds, the class of superaromatic clusters obeying Wade's rule (the $2n + 2$ rule) has been isolated. The structures of transition metal clusters M_n with $n = 3$-38, including small, trigonal-bipyramidal, and octahedral clusters, polyhedra of medium dimensions, and large clusters, are considered and the applicability of the existing schemes to the determination of magic numbers for each of these groups of compounds is discussed.
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I. INTRODUCTION

The present state of transition metal cluster chemistry can be best defined as the stage involving a vigorous search for regularities in order to arrange systematically and explain the entire extensive and varied experimental data. The unusual structure of the polyhedra made up to metal atoms in cluster molecules, the existence in the latter of a new type of bonding not observed in classical chemistry, and the increasing prospects for the use of clusters in catalysis—all these factors have been responsible for the continued rapid expansion of synthetic and structural research in this field.[1-9] Questions concerning the electronic structure of transition metal clusters[10] and related polyhedral molecules[11] have been frequently discussed also in Soviet chemical literature.

At the same time current theoretical ideas in cluster compound chemistry do not yet enable experimenters to predict the structures and reactivities of most of the newly obtained clusters and to estimate even in broad outline the most probable composition of the products of the reactions involving polynuclear molecules. The first fundamental studies designed to find correlations between the stoichiometry of cluster compounds and their geometrical and electronic structures were published more than ten years ago,[2,3] but the task of constructing a non-contradictory theory of the chemical bonds in clusters is still (despite the large number of studies carried out in recent years) far from complete and each of the existing theoretical concepts can account for the experimental facts relating to only a comparatively narrow class of compounds and is usually not concerned with the discussion of the numerous exceptions to a particular suggested rule. We therefore thought it timely to write this review, with the aim of introducing the reader to the range of theoretical problems in cluster chemistry, to give a critical survey of the existing models of the electronic structure of cluster compounds, and to define the limits of applicability of these models on the basis of experimental data.

The first part of the review deals with the theoretical schemes for the electronic structures of transition metal clusters current in the present-day chemical literature, while in the second predictions based on these theoretical schemes are compared with existing structural data. Among theoretical studies, those of a generalising character as well as calculations of the electronic structures of specific clusters, which enabled their authors to reach conclusions applicable to a certain group of polynuclear compounds, were considered in the first place. According to the estimates in Raithby's review,[7] the number of structural studies already exceeded 400 by 1980 and has continued to increase rapidly, which makes an exhaustive consideration of ali the available X-ray diffraction data cumbersome and obsolescent. We have therefore carried out a compilation of structural clusters only to the extent that this has been necessary to illustrate the adequacy or inadequacy of theoretical models for such clusters and the compilation embraces mainly recent studies.

II. QUALITATIVE THEORETICAL SCHEMES FOR THE ELECTRONIC STRUCTURES OF CLUSTER COMPOUNDS OF TRANSITION METALS

The primary task in the chemistry of cluster compounds has been from its inception the explanation of the clear preference for the formation of specific metallopolyhedra containing so-called "magic numbers" of valence electrons. Subsequently, we shall use the term "magic numbers" of electrons in the clusters (the valence electrons) determined from the stoichiometry of the latter as well as electrons assigned to the molecular orbital subsystem characteristic of the clusters—the so-called "skeletal" electrons (see below). These magic numbers have proved in many instances to be a stable characteristic of clusters differing in composition but having similar structures, i.e. a characteristic of a given classified metallopolyhedron. Thus in the majority of trinuclear clusters a closed triangular fragment M_3 (where M is a transition metal) contains 48 valence electrons, a 60-electron configuration is typical for tetranuclear tetrahedral clusters, an 86-electron configuration is typical for hexanuclear octahedral clusters, etc. The total number of valence electrons is then determined in accordance with the scheme usual in organometallic and coordination chemistry: the number of electrons provided by all the ligands in accordance with the usual rules

and in the case of charged clusters also the charge with the sign reversed are added to the total number of electrons in the valence shells of the atoms forming the cluster.†

The molecular orbital (MO) schemes widely employed in the chemistry of organometallic and complex compounds have been used since the beginning of the 1960's to interpret the electronic structure of clusters and to justify their magic numbers.[12,13] These schemes, to be referred to in the subsequent exposition as qualitative (bearing in mind their descriptive character), have remained hitherto the principal element of theoretical analysis in the chemistry of clusters—frequently owing to the difficulty of rigorous quantum-chemical calculations but in the first place because of the possibility of discovering in the simple model the fundamental properties of the molecule. However, the principle underlying the construction of the MO scheme is different in different approaches.

In its classical form, the diagram of one-electron levels of the cluster is constructed from the atomic orbitals (AO) of its constituent metal atoms and the frontier orbitals of the ligands which are used to make up linear combinations transformed in accordance with the irreducible representations of the symmetry point group of the molecule. The relative positions of the energy levels are then determined on the basis of particular qualitative (in reality rather intuitive) considerations. This approach, which was common in the chemical literature of the 1960's and is still sometimes used, appears, however, to be rather useless for the mononuclear transition metal complexes; in reality the number of MO is too large to regard any one of their dispositions as uniquely correct without resorting to additional data. It is therefore not surprising that the molecular-orbital models of the electronic structure of polynuclear complexes almost always involve an appeal to the results of calculations mostly carried out by the extended Hückel method (EHM). The models, with the aid of which certain important generalisations have been achieved, will be examined below in order of increasing complexity.

1. Clusters with Localised Bonds and the Effective Atomic Number (EAN) Rule

Soon after the start of systematic studies on clusters with carbonyl and olefin ligands, it was established that the magic numbers for some of them can be readily obtained by extending Sidgwick's rule [the 18-electron shell or the effective atomic number (EAN) rule] to some of them. This extension is based on the important postulate of the localised, i.e. two-electron two-centre, character of the metal–metal bonds in the polynuclear derivatives considered. Clusters satisfying this postulate are illustrated in Fig.1, which also presents the corresponding numbers of valence electrons N_{val}.

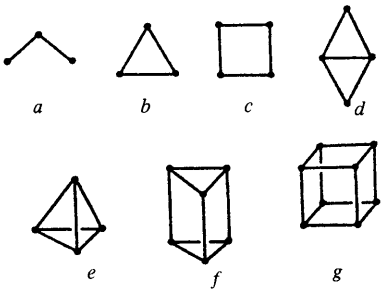


Figure 1. Clusters satisfying the EAN rule and the numbers of valence electrons N_{val} in their metallopolyhedra: *a*) $Os_3(CO)_{10}(\mu_3\text{-}Br)_2$,[15] 50ē; *b*) $Fe_3(CO)_{12}$,[14] 48ē; *c*) $Pt_4(OAc)_8$,[16] 64ē; *d*) $[Re_4(CO)_{16}]^{2-}$,[17] 62ē; *e*) $M_4(CO)_{12}$ (M = Co or Rh),[18] $Cp_3Cr_3Co(CO)(\mu_3\text{-}S)_4$,[19] 60ē; *f*) $[Rh_6C(CO)_{15}]^{2-}$,[20] 90ē; *g*) $Ni_8(CO)_8(PPh)_6$,[21] 120ē (OAc = $OOCCH_3$, Cp = $\eta^5\text{-}C_5H_5$).

The approach based on the EAN rule in essence reduces the electronic structure of clusters to the structure of their simplest analogues—organic or inorganic compounds (tetrahedrane, cubane, prismane, etc.—see Fig.1).# This analogy has been justified also in quantum-chemical calculations: many workers[3,22–25] have established that in model "naked" clusters M_n with M–M distances amounting to 2.5–3.0 Å and characteristic of real transition metal clusters, the splitting of the AO of the *d* block as a result of the formation of metal–metal bonds is insignificant compared with the splitting of the *s* and *p* AO of the valence shell. As a consequence of this, the *s* and *p* AO of the metal atoms make a dominant contribution to the bonding orbitals of the cluster and also to its high antibonding molecular orbitals, the filling of which with electrons leads to the breakdown of the M_n polyhedron. Thus in the stable M_4 tetrahedron with six localised metal–metal bonds the six corresponding antibonding MO should remain vacant, which in fact accounts for the magic numbers for this cluster: $N_{val} = 60$ ($18 \times 4 - 2 \times 6 = 60$).

The EAN rule makes it possible to isolate from the multiplicity of polynuclear complexes and clusters polyhedra related to skeletal compounds in organic chemistry. It is important to note that not more than three edges converge in the vertices in all the clusters illustrated in Fig.1. This geometrical characteristic of clusters with localised bonds probably has a profound topological significance.

†Another scheme for counting electrons in which one begins with a formal ionic structure for the complex and a d^n configuration usually attributed to the residual valence electrons in the transition metal, is current in inorganic chemistry. Clearly there is a rigorous relation between the total number of electrons in the cluster in such an "inorganic" scheme and the total number of valence electrons of the cluster determined in accordance with the "organometallic" scheme, but the numbers are different. This self-evident factor is sometimes forgotten in the consideration of cluster systems, the number of *d* electrons of the model ion (d^n) being used incorrectly in Wade's scheme (see Section II below). The "inorganic" scheme is usually employed in studies of the structure of clusters with halide ligands; in the chemistry of carbonyl clusters and their derivatives, the total number of all the valence electrons is usually considered. To avoid confusion, we shall use in the subsequent exposition only the "organometallic" approach (with the exceptions examined in subsections 1 and 3 of Section II).

#In contrast to skeletal organic compounds, the atom of a light element (H or C) can be incorporated in trigonal-prismatic metal clusters {as in the 90-electron cluster $[Rh_6C(CO)_{15}]^{2-}$ (Fig.1)}. In such derivatives the inserted atom supplies to the polyhedron all the electrons of its valence shell to be used for bonding.

2. Clusters with Many-Centre Bonds and the 2*n* + 2 Rule

Despite its simplicity and effectiveness, the EAN rule is unfortunately not entirely general and embraces only one class of polyhedra with localised metal–metal bonds. On the other hand, structural and chemical studies have made it possible to establish umambiguously that the chemical bond in the majority of cluster compounds is delocalised (many-centre) and does not reduce to the sum of two-centre two-electron interactions.[2] Thus, by placing along each edge of the polyhedron a two-centre two-electron bond even in hexanuclear octahedral clusters, we obtain 12 antibonding MO, the condition for the latter being unoccupied requiring the presence of 84 valence electrons in the cluster ($18 \times 6 - 2 \times 12$), while a magic number of 86$\bar{e}$ is characteristic of the vast majority of such clusters with carbonyl and olefin ligands. On the other hand, another hexanuclear cluster (a trigonal prism) does indeed have $N_{val} = 90$ ($18 \times 6 - 2 \times 9$) in conformity with EAN rules. Thus the transition from a polyhedron with third-order vertices, i.e. vertices joined to three other vertices (for example a trigonal prism), to a polyhedron with fourth-order vertices (for example, an octahedron) alters radically the character of the chemical bond in the cluster.

A magic number of 86$\bar{e}$ was noted in the 1960's virtually in each structural study on octahedral transition metal clusters (see, for example, Cotton and Haas[12] and Corey et al[13]), usually illustrated by a qualitative MO scheme in which numerous electronic levels, both degenerate and non-degenerate, are considered. A logical explanation and a scheme permitting the calculation of the magic numbers for clusters of a specific type with an arbitrary number of vertices were first proposed by Wade.[2,26] In his studies, initially devoted to the electronic structure of polyhedral boron hydrides and carbaboranes,[26] these compounds were subsequently proposed as a correct model for the description of the bonding in metal clusters with electron delocalisation—just as the skeletal organic molecules indicated above can serve as models for clusters satisfying the EAN rule.

Wade's scheme is based on the extremely important hypothesis that the electron system of the polyhedral molecule (carbaborane or metal cluster) is divided into two independent subsystems: the exopolyhedral and skeletal subsystems, which greatly resembles the familiar differentiation of the σ- and π-electron systems in planar aromatic molecules. Such subdivision was first established as a result of quantum-chemical calculations for the simplest polyhedral boron hydrides.[27] The calculations showed that polyhedral molecules with *n* vertices and triangular faces (*closo-n*-gons or deltahedra) contain *n* + 1 bonding MO made up predominantly of the AO of the atoms in the polyhedral skeleton distributed in the scheme in the "upper" (with a higher energy) part of the block of the bonding MO and separated from the antibonding MO by a considerable energy gap.

After comparing the results of structural and computational studies, Wade proposed the "2*n* + 2" rule,[26] according to which any *closo-n*-gon contains *n* + 1 skeletal bonding MO in which 2*n* + 2 skeletal electrons can be accommodated after the attainment of the closed configuration. The presence of a non-triangular ("open") face leads to an increase of the number of skeletal bonding MO by one and hence to the existence of 2*n* + 4 skeletal electrons in the *nido-n*-gon with one open face, of 2*n* + 6 skeletal electrons in the *arachno-n*-gon with two open faces, of 2*n* + 8 skeletal electrons in the *hypho-n*-gon with three open faces, etc. The appearance of a "cap", i.e. of an additional vertex located above the triangular face, in the polyhedron, which is frequently observed in metal clusters, does not increase the number of skeletal MO of the main polyhedron and the number of skeletal electrons supplied by this vertex is calculated in the same way as for the other vertices in metal clusters. The additional atom inserted into the polyhedral cavity also does not alter the number of skeletal MO and supplies its valence electrons to the skeletal bonding system in the cluster.

The scheme which Wade proposed[26] for counting electrons in a cluster employs the additional postulate of the involvement of three AO of the atom occupying the vertex of the polyhedron and the formation of skeletal MO. In the exopolyhedral system of orbitals of this atom (which is responsible for bonding with the ligands and which accommodates the unshared electron pairs) there remain respectively one AO in the case of a non-transition element and six AO in the case of a transition element. Thus the number of electrons introduced into the polyhedron for "skeletal" bonding by the mononuclear fragment located at its vertex is $x + l - 2$ for an atom of a non-transition element at the vertex of the polyhedron and $x + l - 12$ in the case of a transition metal atom, where x is the number of valence electrons of the given atom and l the number of electrons supplied by the ligands bound to the given atom.

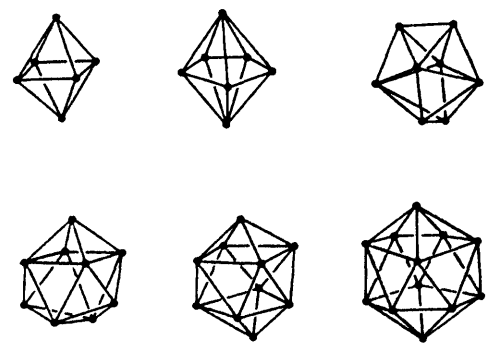


Figure 2. Types of metallopolyhedra in clusters with delocalisation of skeletal electrons.

According to this scheme, the $(OC)_3Fe$ and CpCo fragments each supply two electrons to the skeletal bonding system of the polyhedron, while the $(OC)_3Co$ fragments supply three electrons—in the former case analogously to the BH fragment and in the latter analogously to the CH fragment. The total number of skeletal electrons in an *n*-nuclear homoatomic cluster made up of transition metal atoms is then $n(x + l - 12) - q$, where q is the charge of the cluster, and is related to the number of vertices and open faces of the polyhedron by Wade's rule. The number of skeletal electrons can be found from the number of valence electrons and conversely (in the case of clusters made up of transition metal atoms $N_{val} = N_{sk} + 12n$, where n is the number of transition metal atoms). Thus octahedral clusters with 86 valence electrons contain 14 skeletal electrons, i.e. $86-12 \times 6$, in conformity with Wade's rule (*closo*-6-gon, $2n + 2 = 2 \times 6 + 2$). The magic number 86$\bar{e}$ for an octahedral cluster has thus been accounted for.

The 2*n* + 2 rule and the associated scheme for the counting of electrons, nowadays frequently referred to as the theory of skeletal electron pairs, has made a significant contribution to the theoretical ideas in the chemistry of clusters. The similarity of the structures of metal clusters and polyhedral

molecules such as those of boranes, carbaboranes, metalloboranes, and metallocarbaboranes, π-complexes, and nonclassical cations has been established on their basis.[2,3] With the aid of the $2n + 2$ rule, chemists have been able to predict the structure of a cluster on the basis of its stoichiometric composition.

The relation between the $2n + 2$ and EAN rules can be readily accounted for in terms of the postulate, adopted by Wade, that three AO of the atom at the vertex are involved in polyhedral skeletal bonding. Conditions for the formation of localised bonds are indeed fulfilled in clusters where all the vertices have an order $n \leq 3$ as a consequence of the overlap of the AO of neighbouring vertices in pairs. An increase of the order of the vertices in the polyhedron leads to a delocalised skeletal bonding system. Examples of the polyhedra encountered in the structures of carbaboranes and metal clusters are illustrated in Fig.2. We may note that the vertices of all these polyhedra have an order of four and above.

3. Lauher's CVMO Scheme and Other Approaches Based on EHM Calculations

The $2n + 2$ rule, which makes it possible to treat systematically the structures of a large number of clusters, has now become widely popular. The region of its applicability has proved, however, to be restricted to polyhedra of medium size, mainly made up of the atoms of Fe, Co, and their analogues with carbonyl ligands, some of which can be substituted by other "soft" ligands. Thus numerous clusters of other types remained outside the limits of Wade's scheme. Furthermore, Wade's rule itself is more in the nature of an empirical generalisation, leaving room for further development of the theory. The latest studies in the theoretical chemistry of clusters have accordingly developed in two directions: in ne of these the aim was to seek analogous schemes for the counting of electrons in other types of clusters and in the other the aim was to find a theoretical justification of the validity of the $2n + 2$ rule. In this subsection we shall consider the most widely used schemes developed in accordance with the first approach, while in the next subsection the results of the development of the second approach will be described.

The close relationship between clusters with localised and delocalised bonds which follows from the $2n + 2$ rule justifies the application to the latter of the model which made it possible previously to extend the EAN rule to clusters with localised bonds. According to this model, which we examined above, the highest antibonding MO of an isolated polyhedral M_n fragment are most important for the description of the electronic structure and for the determination of the magic numbers of the cluster; the filling of these MO by electrons is accompanied by the disruption of the cluster structure.[3,22] In contrast to clusters with localised bonds, such MO cannot be clearly represented by the sum of two-centre interactions; furthermore, for clusters of arbitrary type no *a priori* considerations are known at present which would permit a rigorous determination of the number of these MO. The significantly many-centre character of the bond in the clusters considered has given rise to a tendency to construct "canonical forms" with three-, four-, six-centre, etc. two-electron bonds and the resonance between such forms can evidently account for any number of valence electrons observed in reality. However, the predictive power of this scheme, described in Johnson and Benfield's review,[6] appears to us to be extremely insignificant, because procedures for a quantitative estimation of the contributions of the canonical forms considered to the overall resonance hybrid are not then defined (on the other hand, the main part of Johnson and Benfield's review,[6] devoted to studies of the configurations of ligands in carbonyl clusters, is extremely relevant and interesting). An attempt may be made to obviate the difficulties caused by the lack of rigorous theoretical principles for the prediction of the number of configurations of the antibonding MO of the cluster by constructing a MO diagram with the aid of quantum-chemical calculations. The first important results on these lines have been obtained by Mingos,[3] who confirmed by means of EHM calculations the validity of the selection of polyhedral B_6 molecules as a model of the Co_6 cluster. The calculated disposition of the highest antibonding MO made up of s and p AO in the B_6 and Co_6 clusters is indeed the same (Fig.3); the MO of the $3d$ type in the Co_6 cluster then constitute an extremely narrow band as a consequence of the less effective overlap of the corresponding AO.[3] The diagram obtained illustrates satisfactorily the applicability of the $2n + 2$ rule, derived for carbaboranes, to clusters of the metals in the centres of the transition series.

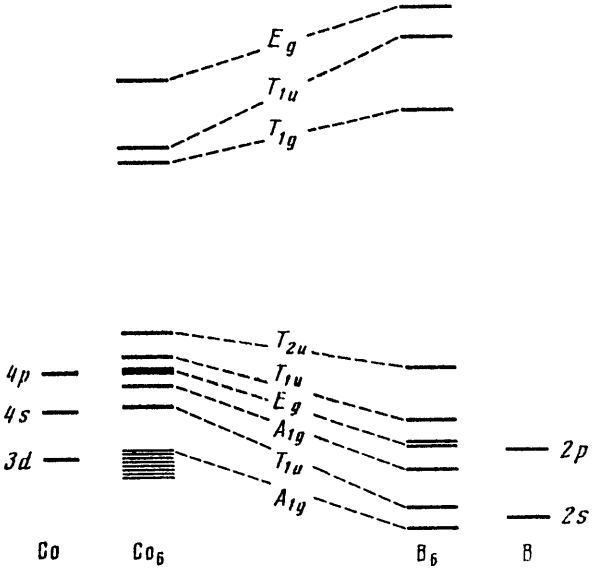


Figure 3. MO schemes for model Co_6 and B_6 clusters.[3]

The next step in the analysis of the MO with an isolated metal cluster was the scheme proposed by Lauher in a series of communications,[22,23] which is frequently referred to as the theory of valence MO of the cluster (CVMO) or of the valence electrons of the cluster. Lauher's scheme divides the MO of the cluster into low-lying CVMO and the antibonding MO (HLAO), designated here by AMO, separated from them by an energy gap. When ligands are coordinated to the cluster nucleus, the CVMO are modified as a consequence of their involvement in bonding while the AMO undergoes smaller changes (owing to the greater difference between their energies and those of the ligand orbitals) and remain unoccupied in the molecule of a real cluster. After differentiating the AMO on the molecular orbital diagram of the M_n cluster, calculated with the aid of EHM, the magic numbers of electrons

which can be accommodated in the CVMO of the given polyhedron when it is coordinated to the ligands are obtained. Specific calculations enable the author[23] to introduce the following semiquantitative criterion for the separation of the AMO from the CVMO: the antibonding MO of the cluster usually have higher energies than the unoccupied p AO of the metal atom.[23]

In contrast to Wade's scheme which operates with the intrapolyhedral (skeletal) electronic configuration, Lauher's scheme includes all the valence electrons of the cluster and is applicable in principle to metallopolyhedra having structures of any complexity, provided that the computational method employed in the scheme is sufficiently correct. Although a useful aspect of the qualitative scheme, namely the possibility of finding the magic number for a polyhedron of any structure without quantum-chemical calculations, is lost in this approach, it also makes it possible to determine the number of valence electrons in a specific M_n cluster with an arbitrary disposition of ligands in terms of a uniquely calculated MO scheme, although it does not provide a unique explanation of such numbers. On the other hand, in his first study,[22] Lauher reproduced, for example, the stable 170-electron configuration of the $[Rh_{13}(CO)_{24}H_3]^{2-}$ cluster with an Rh atom incorporated within the polyhedron, which cannot be interpreted in terms of other schemes, and carried out calculations for a series of M_n clusters with $n = 3 - 15$.

The total number of CVMO is expressed in Lauher's method as $6n + X$, where X is a quantity which assumes values from 3 to 13 depending on the geometry of the M_n polyhedron. The number of CVMO corresponding to one metal atom varies in conformity with this, converging slowly to 5.3, a value characteristic of an infinite metallic lattice, as the size of the cluster increases.

It appears that the CVMO scheme still suffers from the disadvantage that the prediction of the order in which the MO of the cluster are distributed on the basis of qualitative considerations is difficult and hence the results depend on the adequacy or inadequacy of the computational method employed. The extended Hückel method employed by Lauher (the simplest and therefore hitherto the only semiempirical quantum-chemical method used in calculations for systems such as polynuclear transition metal clusters) is by no means universal; its fundamental validity has been questioned even in calculations for mononuclear transition metal complexes.[28] An advantage of the EHM is that it takes into account the topology of the molecule by introducing into the matrix of the model Hamiltonian non-diagonal elements proportional to the overlap integrals. However, the question of the applicability of the given method to calculations for the molecules of organometallic and also cluster compounds is complex and requires further investigation.

In Lauher's study[22] the CVMO scheme reproduced correctly, in conformity with the predictions of the EAN or $2n + 2$ rule, the magic numbers for a series of common polyhedra (tetrahedron, trigonal prism, octahedron, cube, two-cap Archimedes antiprism, eicosahedron). However, results in conflict with the existing qualitative schemes and inconsistent with the magic numbers of the carbaborane analogues have been obtained for certain polyhedra (pentagonal pyramid, dodecahedron with trigonal faces, and square antiprism without caps). It is of interest to note that the real structure of transition metal clusters with such polyhedra of medium dimensions exhibits in reality deviations also from the predictions based on the $2n + 2$ rule, although this structure is not in fact fully consistent with Lauher's magic numbers either (see section II). For the octahedron with four caps, located in accordance with a tetrahedral motif, the predictions of the CVMO scheme ($N_{val} = 140$) have also not been confirmed: the corresponding osmium clusters of the type $[Os_{10}C(CO)_{24}]^{2-}$ contain 134 valence electrons in conformity with Wade's scheme.[29]§

The advantages and disadvantages of Lauher's approach are well illustrated by a study of Italian workers,[24] who quote the results of the calculation for more than 100 M_n metal clusters containing fragments of close-packed metal atoms. Calculation for eight Rh clusters of known structure, which served as models, made it possible (in some conflict with Lauher's data) to specify unambiguously the set of CVMO, corresponding to the real number of valence electrons, only for the three polyhedra of highest symmetry. In the remaining cases the numbers of valence electrons predicted did not agree with the real composition or a uniform distribution of levels was observed on the MO diagram, so that their separation into CVMO and AMO with respect to the energy of an isolated metal atom proved to be fairly arbitrary. In order to reduce the discrepancies between the calculated and observed numbers of electrons in planar trinuclear and tetranuclear clusters, it was necessary to choose as the AMO the orbitals whose energies were much higher than that of the unoccupied p level. Nevertheless, the authors[24] believe that the agreement between the calculated and experimental magic numbers is adequate for a qualitative consideration of the structure of transition metal clusters.

The numbers of CVMO determined by the above investigators[24] correspond to the formula $6n + X$ where X varies from 6 to 11. $X = 7$ was found for approximately half of the structures for which calculations had been made and $X = 8$ was found for one-quarter of the structures. Since the formal validity of the $2n + 2$ rule requires the existence of $2n - 1$ skeletal AMO and correspondingly $7n + 1$ CVMO, the authors[24] concluded that Wade's rule is inadequate for the class of systems which they investigated and proposed a $6n + X$ rule for an arbitrary n-atomic cluster, where in the majority of cases $X = 7$. This modification of Lauher's formula, which has been quoted recently in a number of communications, is in our view erroneous. The discrepancy between the number of CVMO of an n-vertex cluster and the

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§ In certain recently published communications (B.K.Teo, Inorg.Chem., 1984, **23**, 1251; B.K.Teo, G.Longoni, and F.R.K.Chung, Inorg.Chem., 1984, **23**, 1258) the number of CVMO of an arbitrary M_n metal cluster has been determined without a preliminary calculation, solely on the basis of the EAN rule and Euler's theorem by means of the formula $8V + 2 - F + X$, where V is the number of vertices of the cluster, F the number of its faces, and X the number of "additional" electron pairs necessary to create a stable electronic configuration, in excess of the number required in accordance with the EAN rule for a cluster with localised M–M bonds. The introduction of the term X reflects the many-centre character of the bonding in the cluster; $X = 0$ in all polyhedra with third-order vertices. The values of X for stable clusters, including those made up of several polyhedra, are determined by a set of seven rules (supported by a qualitative examination of the MO). These rules make it possible to find the numbers of valence electrons N_{val} for a large number of clusters with carbonyl ligands which have been investigated. The discrepancies between the calculated and real values of N_{val} are then observed mainly for cluster compounds of the elements at the end of the transition series and for the majority of metal clusters. The empirical character of the rules, which frequently specify 2–3 magic numbers of valence electrons for the metallopolyhedra most frequently encountered (trigonal bipyramid, octahedron, the Archimedes antiprism, and a three-cap triangular prism) can apparently be regarded as one of the disadvantages of the proposed scheme.

"Wade" value of $7n + 1$ can in general indicate the inapplicability of the $2n + 2$ rule to the given polyhedron, because the rule is not universal. However, $X = 7$ is also not of general validity (see Table 2 in Lauher's paper[22]) and its frequent appearance in the results of calculations reflects mainly the fact that more than half of the metal clusters considered[24] are constructed on the basis of an octahedron or a tetragonal pyramid supplemented by different numbers of "caps" or other condensed polyhedra. In conformity with Wade's rule, the octahedron (*closo*-hexagon) or tetragonal pyramid (*nido*-pentagon) with an arbitrary number of caps should have seven skeletal electron pairs, which, when added together to the $6n$ exopolyhedral MO, yields precisely $6n + 7$ CVMO. In this case X is exactly equal to 7 (Wade's formula includes the number of vertices not centred on trigonal faces and not the total number of vertices of the polyhedron[2]).

The results of the above study[24] illustrate in a somewhat unexpected fashion the, on the whole, correct evaluation of the number of CVMO (and hence of the valence electrons) by EHM calculations for clusters where they can be calculated independently in accordance with the $2n + 2$ rule. However, for a series of clusters including the four-cap octahedron discussed above, numbers N_{val} inconsistent with the real values (see Section III) were obtained. The reasons for the adequacy of the computational scheme under consideration in the case of some polyhedra and its inadequacy for their closest analogues are not entirely clear and we believe that so far the results of EHM calculations should be treated with a certain amount of caution.

It might have been expected that the results of EHM calculations will become more applicable with increase of the number of atoms in the cluster and on transition to an infinite crystal lattice of the metal in the limit, because in this region of large clusters the qualitative chemical rules governing the electronic structure are so far unknown. However, in calculations for large M_n metal clusters with $n = 16$–22[22,24] it was shown that, with increase of the number of metal atoms, the MO system approaches ever more closely the continuous region where no subdivision into AMO and CVMO is observed.

The CVMO method has been criticised also from the standpoint of a physical approach in which clusters are treated within the framework of band theory. According to Wooley,[9] who describes the physical point of view on clusters, the extended Hückel method yields an unduly small d band width in polyatomic transition metal aggregates (~1 eV in Mingos's calculations and ~3eV according to the estimates of band theory) and generates a bonding pattern inconsistent with the limiting case of a metallic lattice in which the bonding electrons occupy the d band and the s and p electrons (the probability of finding such electrons in the inner shells of a neighbouring atom is not zero as a consequence of the diffuseness of the corresponding AO) are antibonding because of orthogonality factors. There is no doubt about the value of the approach to the structures of large metal clusters from the standpoint of the ideas of solid state physics (band theory), but one should note that in this field the interests of physicists and chemists sometimes do not coincide and studies of correlations of the "composition–structure–properties" type must nevertheless be based on theoretical considerations derived from fairly approximate chemical models.

As in other theoretical schemes in the chemistry of clusters, the CVMO method is not universal even when the EHM calculation is correct.[23] In particular, with its aid it is impossible to interpret the electronic structures of polynuclear platinum and gold compounds (although these admittedly cannot be described satisfactorily within the framework of other theoretical schemes either). Thus the octahedral cluster $\{Au_6[P(C_6H_4Me)_3]_6\}^{2+}$, containing 76 valence electrons, i.e. four skeletal electrons, does not fit any of the existing models.

The electronic structures of the numerous unusual platinum and gold clusters obtained in recent years have been interpreted by Mingos using the results of EHM calculations.[31–36] Gold clusters of medium dimensions ($n = 6$–13) have been considered taking into account two findings by the same investigator: (1) the slight overlap of the occupied d AO leading to the formation of a narrow d band of a weakly antibonding character and (2) the small contribution of high-energy unoccupied p AO of the Au atoms to the bonding in the cluster. As a zeroth approximation, Mingos adopted a simplified model taking into account only the interaction of the valence s AO of the Au atoms in the clusters; in essence, this model is analogous to that of the simple Hückel method, where account is taken only of the overlap between the orbitals of neighbouring atoms and the p AO of the π-system are replaced by the s AO of the atoms making up the polyhedron.[31] The simple orbital diagram obtained for this model agrees with the relative disposition of the s MO in a more complex schematic arrangement of levels calculated using valence s, p, and d AO as the basis. The s MO schemes for the octahedral and eicosahedral clusters are presented in Fig. 4.

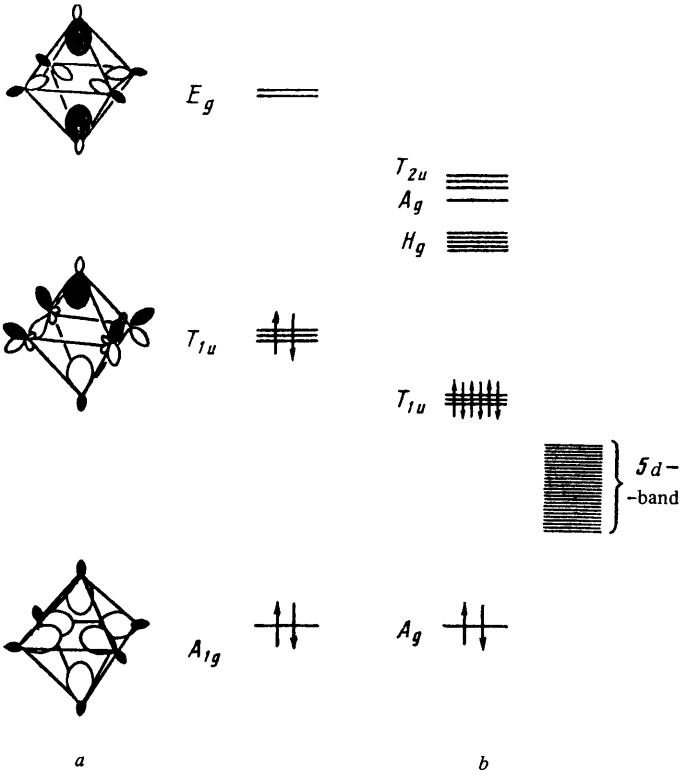


Figure 4. MO schemes for the Au_6 octahedral cluster (a) and the centred Au_{13} eicosahedral cluster (b).[31]

Mingos[31] demonstrated that the structures of the Au_n clusters based on a centred eicosahedron with the greatest contribution to the bonding by the interaction between the central and peripheral Au atoms are preferable. The coordination of n phosphine ligands at the vertices of such a

polyhedron results in the formation of n strongly bonding MO of the exopolyhedral type and the corresponding increase of the energy of the cluster s MO with retention of their relative positions.

The stable electronic configuration predicted by this calculation corresponds to the composition of the $[Au_{13}(PPh_3)_{12}]^{5+}$ cluster. This prediction was confirmed by the successful synthesis of the isoelectronic cluster $[Au_{13}L_{10}Cl_2]^{3+}$ with the *trans*-disposition of the Cl ligands in the eicosahedron.[32] Calculations for the octahedral $[Au_6L_6]^{2+}$ cluster predict an open electron shell [only two electrons are located in the triply degenerate T_{1u} MO (Fig. 4)], which subsequently led Evans and Mingos[33] to doubt the validity of the structural study of Bellon et al.[30] and the correctness of the composition established. The prediction of the stability of the octagonal dodecahedral Au_8C clusters with a carbide carbon atom at the centre of the polyhedron[31] has not so far been confirmed experimentally.

In the theoretical schemes examined above the cluster molecule is subdivided into the metallopolyhedron proper and its ligand environment and the electronic characteristics of the polyhedron, which depend little on the configuration of the ligands, are analysed. There exists also an alternative approach to the determination of the electronic structure of the clusters in which the MO scheme for the polyhedral molecule is constructed from the frontier orbitals of the mononuclear ML_k fragments. The idea, that the fragments of different nature whose frontier orbitals have similar energies and have the same nodal properties are stereochemically similar, occupies a major place in this approach. These considerations are to some extent already contained in Wade's classification of the mononuclear fragments of the cluster in terms of the number of electrons which they supply to the polyhedron, have been generalised in the familiar principle of isolobal correspondence,[36] and are widely used in interpreting the results of EHM calculations.[33–35] In this interpretation the analogy between the metal carbonyl clusters and polyhedral boranes and carbaboranes is justified by the isolobality of the $M(CO)_3$ and MCp fragments (where M is a transition metal) in relation to the BH and CH fragments. The development of schemes for the counting of electrons in polyhedral molecules outside the region of applicability of the EAN and $2n + 2$ rules, in this type of treatment is an expected result of the analysis of the correlation diagram of a cluster made up of mononuclear fragments such as $M(CO)_4$, ML_2, or ML, where L is a phosphine ligand, which are not isolobal with respect to the BH group. The last two fragments are encountered mainly in "non-Wade" Pt and Au clusters respectively; the magic numbers for small polyhedra with the number of vertices n between 3 and 6, which have been proposed on the basis of EHM results, were interpreted on the basis of the isolobal analogies of the given fragments.[33–35]

Nevertheless, the calculations have demonstrated the absence of adequate models for the AuL or PtL_2 fragments among the compounds of other elements. In the case of small Pt clusters, the electronic structure and the magic number derived from it proved to be different for different orientations of the ligands L relative to the Pt_n metallopolyhedra.[34] On the other hand, the energy of formation of Au clusters of different structure proved virtually identical in EHM calculations.[33] The isolobal analogy between the $Pt(PH_3)_2$ "corner" fragment and the $M(CO)_3$ "conical" fragment proved to be incomplete as a consequence of the energy splitting of the $hy(xz)$ hybrid orbital and the $p(y)$ atomic orbital, whose equivalents are degenerate in the case of $M(CO)_3$ (it is of interest to note that the frontier orbitals obtained in the studies quoted usually contain a significant contribution from d AO). The isolobal correspondence between the $AuPR_3$ fragment and the hydride ligand H has been postulated[33] for small Au clusters. It was deduced from structural data for the mixed clusters of the type $Os_3(CO)_{10}\cdot(AuPEt_3)_2$ [37] and $Ru_4(CO)_{12}(AuPR_3)_3H$, [38] where the $AuPR_3$ fragment as it were occupies the place of the μ-H ligand in the hydride derivatives, which have been synthesised recently. However, this analogy is incomplete and the authors stipulate the possibility in principle of the involvement in bonding also of the 6p AO of the Au atoms.[33]

On the whole, we believe that, with all its undoubted clarity and popularity, the analysis of the frontier orbitals of the fragments is in essence insufficiently effective for the prediction of the characteristics of the structure of polyhedral molecules which are at present not susceptible to description in terms of other schemes. The results of a number of studies[33–36] represent essentially the expression of experimental structural data in terms of frontier MO schemes and their explanation on the basis of a more detailed specification of the postulates which had already been put forward in earlier studies[31] and which involves certain controversial claims—the existence of two instead of three metal–metal bonds in 44-electron trinuclear Pt complexes[35] in the presence of 54 instead of 58 valence electrons in the $Au_4(\mu\text{-}I)_2(PR_3)_4$ tetrahedral cluster.[33] There is no doubt that consideration of a specific type of MO of the clusters gives rise to extensive possibilities for the interpretation of experimental data but the value of the theoretical scheme is largely determined by its predictive power. We believe that in this sense the principle of isolobal correspondence, which is extremely useful for the systematic treatment of a large number of molecular structures, may in many instances prove to be relatively inapplicable to the real structural-chemical problem.

4. The Topological Interpretation of the Electronic Structure of Cluster Systems

The ideas borrowed from topology and the graph theory have nowadays penetrated structural and quantum chemistry to an increasing extent. The development of studies on cluster molecules and the wide variety and unusual nature of the polyhedra present in them have led to a kind of fascination with the topological terminology, the employment of which in most of the studies published hitherto makes the interpretation of the results more novel than fruitful. Advances in theoretical chemistry and in the first place the study of the MO of planar aromatic systems by the graph theory method[39] have shown, however, that the application of the procedures of this, one of the most modern and abstract fields of mathematics, to chemical problems can be extremely useful and the possibilities for the introduction of topological ideas into the chemistry of cluster molecules are apparently much wider than the mere determination of the number of edges from the number of faces (or conversely) in an n-vertex cluster in terms of Euler's scheme. Topological ideas have been used to some extent in studies carried out in recent years whose aim was a theoretical justification of the $2n + 2$ rule.[40,41]

The book of King and Rouvray[40] deals, like other theoretical studies of the electronic structure of clusters, with a qualitative diagram of the Hückel MO of a polyhedral molecule. The novelty of this study consists in the analysis of the energies of the MO in a polyhedron of arbitrary type of symmetry solely on the basis of a scheme for the chemical bonds present in the molecule (i.e. the molecular graph). This approach is possible because the energies of the levels (i.e. the eigenvalues of the matrix of the model Hamiltonian H) in the Hückel model can be expressed in terms of the eigenvalues of another very simple matrix—the adjoint matrix A of the molecular graph whose elements are 1 for the pair of vertices

joined by a chemical bond and 0 for any other pair of vertices. The set of eigen-values of the adjoint matrix of a cyclic molecular graph C_n defines, for example, the MO diagram for aromatic π-systems, which constitutes the basis of the Hückel rule. The molecular orbital diagrams whereby it is possible to justify the $2n + 2$ rule can be derived analogously from the molecular graphs reflecting the bonding in the skeletal electron system of the cluster.

Starting with Wade's hypothesis of the involvement of three orbitals of the mononuclear fragment of a *closo*-polyhedron in the skeletal bonding system, it has been suggested[40] that two tangential orbitals (of the τ type), located along the tangent to the surface of the polyhedron, and one internal orbital (of the *i* type), directed to the centre of the cluster, be constructed from them. In an *n*-vertex cluster *n* bonding and *n* antibonding τ MO are formed from $2n$ τ AO, while a single bonding and $n - 1$ antibonding MO are formed from *n i* AO (the region of the mutual overlap of which is in the central part of the polyhedron) in conformity with the eigenvalues of the adjoint matrix of the graph of the *i* AO system, which represents the complete graph K_n (each vertex is connected to all the others). The bonding MO, the total number of which is thus $n + 1$, can accommodate $2n + 2$ skeletal electrons, which is consistent with Wade's rule. The cluster with triangular faces, which obeys the $2n + 2$ rule, is regarded as a three-dimensional superaromatic system with electron delocalisation, which represents a generalisation of the π-systems of planar aromatic molecules.

Thus, in addition to Wade's hypothesis of the separation of the exo- and endopolyhedral electron systems, the King and Rouvray scheme considers the τ and *i* MO also as independent of one another. These postulates appear to be fairly natural but cannot be rigorously derived from the symmetry properties of the cluster, which are altogether disregarded in this approach. The appearance of an additional pair of skeletal electrons in clusters with an open face has been justified[40] by introducing yet another hypothesis, this time the hypothesis of the separation of the system of *n i* AO of a *nido*-*n*-gon into the ν orbitals of the atoms surrounding the open face and the $n - \nu$ orbitals of the remaining atoms of the polyhedron. Each of these subsystems is assumed to be represented by its complete graph (K_ν and $K_{n-\nu}$ respectively), as a consequence of which two bonding orbitals of the *i* type arise in the system of skeletal MO instead of one such orbital. The increase of the number of open faces ("breaks") (on a *closo*-surface) as well as the introduction of "caps" in super-electron-deficient clusters lead, according to the authors,[40] to an increase of the degree of localisation of the bonds in the polyhedron.¶

Despite the importance of the results obtained, King and Rouvray's study[40] does not nevertheless provide an exhaustive description of three-dimensional superaromatic systems and does not contain a justification of the extremely significant initial postulates. The authors relate the degree of delocalisation of electrons in the cluster to the fraction of triangular faces on the total surface of the polyhedron, but the physical causes of this relation are not discussed. Finally, the results of graph theory have been applied in this instance only in terms of the simplest quantum-chemical Hückel method.

The strong aspects of the EHM are then clearly revealed: for example, it becomes understandable why calculations of this type have yielded such satisfactory results in the study of the polyhedral $B_nH_n^{2-}$ ions[27] but it has not been ultimately elucidated to what extent the relations obtained depend on the specific method of calculation employed.

Some of the questions enumerated above have been eliminated by Stone,[41] who developed a different much more general and physically well-founded model of the bonding interaction in the cluster. Having refrained from *a priori* assumptions about the number and form of the AO occupied in the exopolyhedral electron system, Stone employed in his study a single postulate, according to which the atoms making up the cluster polyhedron are approximately at equal distances from its centre. On this basis, he constructed a simple model of the polyhedral molecule whose atoms are uniformly distributed on the surface of a sphere. Thus, whereas the molecular symmetry is not considered at all in King and Rouvray's book, Stone's model has a spherical symmetry, which is the highest possible in a three-dimensional space. Nevertheless, with the aid of this model, it is possible to derive relations suitable for any clusters however low their symmetry.

In his study[41] Stone employed the wave function of a spherically symmetrical shell, which can be transformed into $R(r)Y_{lm}(\theta,\phi)$ in terms of polar coordinates, where the angular component Y_{lm} represents spherical functions, well known in quantum mechanics, which are defined in terms of two quantum numbers (the orbital momentum *l* and the magnetic momentum *m*) and which are degenerate by a factor $2l + 1$, like the sublevels of an isolated atom (see, for example, Messia[42]). Stone constructed the wave function of the cluster in accordance with the LCAO MO scheme in the form of a sum of the basis AO of the constituent atoms $\psi = \Sigma c_i\chi_i$; he employed the spherical functions Y_{lm} as the coefficients of the c_i in the expansion of ψ in terms of the basis functions $\{\chi_i\}$. This makes it possible to classify the resulting MO cluster in terms of the quantum number *l*, as is done for an isolated atom, by introducing the one-cluster *S* MO ($l = 0$), the three cluster *P* MO ($l = 1$), the five-cluster *D* MO ($l = 2$), etc. However, not all these MO exist in a specific cluster, because the spherical functions Y_{lm}, which appear in the expansion of the wave functions ψ for certain values of *l*, can become zero at the vertices of the polyhedron.

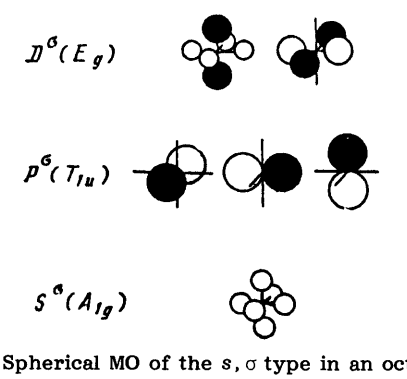


Figure 5. Spherical MO of the s, σ type in an octahedral cluster.[41]

In reality, only *n* linearly independent cluster MO can be made up of *n* basis functions χ_i. Thus it is possible to set up six independent MO of the σ type from six *s* AO of the metal atom (Fig.5): one fully symmetrical S^σ MO, three

¶The method developed by King and Rouvray[40] has been discussed in detail by Yanovskii (see this issue of the Journal). For our purposes, the use of postulates of a topological character in King and Rouvray's proof of the validity of the $2n + 2$ rule rather than the proof itself, is most significant.

degenerate P^{σ} MO antisymmetric with respect to inversion, and two of the five D^{σ} MO, since the other D^{σ} MO become zero (because the corresponding functions Y_{2m} at the vertices of the octahedron are zero).[41] The distribution of the cluster MO in terms of energy can be derived qualitatively from the number of nodal surfaces and is consistent with the usual pattern: the bonding A_{1g} MO, the non-bonding T_{1u} MO, and the antibonding E_g MO for an octahedral cluster (Fig. 4a).

The difference between the MO of a "spherical" cluster and the AO of an isolated atom consists in the fact that they have different forms depending not only on the quantum numbers l and m but also on the types of the basis functions (s, p, and d) and their overlap (σ, π, and δ). Accordingly, it is possible to isolate the following series of levels for a cluster made up to transition metal atoms: S_s^{σ}, P_s^{σ}, D_s^{σ}, ..., S_p^{σ}, P_p^{σ}, D_p^{σ}, ..., P_p^{π}, D_p^{π}, S_p^{π}, ..., P_d^{π}, D_d^{π}, F_d^{π}, ..., D_d^{δ}, δ, G_d^{δ}, ..., etc. The transition from cluster MO of the σ type to the MO of the π and δ types required also appropriate changes in the mathematical procedures, namely the introduction of the corresponding vector and tensor spherical functions instead of the corresponding scalar spherical functions Y_{lm}. The main consequence of such a change is the subdivision of $2n$ linearly independent π or δ MO into n low-energy even (i.e. symmetrical relative to the inversion operation) and n high-energy odd (antisymmetric in relation to inversion) orbitals. Thus pairs of MO made up of the even P_p^{π} and odd $\bar{P}_p^{\pi}$ orbitals, the even D_d^{δ} and odd $\bar{D}_d^{\delta}$ orbitals, etc., in which the first MO is in general bonding while the second is antibonding, appear.

Despite the large number of cluster MO of different types, their relative disposition as regards energy is extremely consistent. Thus, among all the MO of the σ type, only the S_s^{σ} orbital is bonding, while the others are antibonding. In the n-vertex cluster the P^{π} MO are divided into two groups: n even bonding P_p^{π} MO and n odd anti-bonding $\bar{P}_p^{\pi}$ MO, which is analogous to the formation of n molecular orbitals of the τ type and n orbitals of the τ^* type in the book of King and Rouvray. The cluster made up of n atoms of the elements in the Second Period thus contains $n + 1$ bonding MO. The splitting of the even and odd constituent π and δ MO, made up of d AO, is insignificant according to Stone's calculations[41] and all the MO of this type in the cluster are occupied by electrons (as shown above, the same result has been obtained in EHM calculations). Thus in this instance the $2n + 2$ rule has been justified (the presence of n bonding P_p^{π} MO and one bonding S_s^{σ} MO in the cluster). The expression for the bond energy in the cluster based on Stone's model contains a product of the type $Af(\omega)$, where $f(\omega)$ depends solely on the angular distance between neighbouring atoms on the surface of the sphere and the factor A is the ratio of the number of edges of the cluster to the number of its vertices and is a maximum for the *closo*-polyhedron with triangular faces. In this case the preference for cluster *closo*-structures is likewise well-founded.

At first sight Stone's scheme has no bearing on topology, because it uses the spherical shell model, which has been well developed in quantum mechanics. However, the very fact that the systematic treatment of the MO in accordance with the orbital quantum numbers l for an idealised spherical system is applicable to an arbitrary polyhedral molecule apparently demonstrates that the symmetry of the model is not itself of decisive importance in this instance and in a certain sense it merely complicates the description of the bonding, generating a large number of multiplets. Stone[41] emphasises the kinship between the spherical shell model and other simple models of systems with electron delocalisation—such as the linear potential box for conjugated polyenes and a closed conducting ring for cyclic π-systems. The latter model is purely topological: indeed Hückel's rule can be most simply derived for an ideal annular potential box with $D_{\infty h}$ symmetry (the lowest non-degenerate Σ_u level and an infinite sequence of doubly degenerate Π, Δ, etc. levels require the presence of $4n + 2$ π-electrons in a system with paired spins), but it is valid for all planar aromatic molecules however low their symmetry and is determined precisely by the fact that the π-electron system is closed. Analogously the adquacy of Stone's model in describing clusters is apparently determined by the same properties, namely the closed nature of the three-dimensional electron shell of the cluster, its homogeneous conductivity, and the presence of an inner cavity (we may note that the same properties of a superaromatic cluster with the additional hypothesis concerning the number of skeletal orbitals have been used in the studies by King and Rouvray).

In analysing cluster MO, Stone does not consider the consequences of the appearance of open faces in the polyhedron (i.e. the breakdown of the principle of the uniform distribution of atoms on the sphere underlying the model) and in essence proposes the same $2n + 2$ rule for every cluster, beginning with the diatomic molecule (as an example, he considered[41] the N_2 molecule). Despite the use of complex mathematical procedures, the scheme includes also significantly qualitative considerations, which are in many instances resorted to to account for the discrepancy between the predicted and true numbers of valence electrons in the molecule. The postulate of a weak interaction of the MO localised in various regions of the polyhedron (internal, surface, and exopolyhedral), which in fact corresponds to the postulate of the subdivision of the cluster MO into sybsystems (however, with a difference from the studies of Wade[2] and King and Rouvray[40] consisting in the fact that in Stone's work this postulate is a computational fact arising from the proposed model), is of special interest. The subdivision of the MO referring to topologically different regions of the cluster has been confirmed at the present time also experimentally;[9] however, quantum chemistry does not apparently as yet possess mathematical methods suitable for the analysis of this extremely interesting phenomenon.

Thus qualitative MO schemes make it possible not only to bring order into the experimental findings in the chemistry of clusters but also to achieve significant progress in the understanding of the causes of these findings. One may note further that principal advances in the theoretical description have been attained for clusters obeying the $2n + 2$ rule, which are nowadays regarded as three-dimensional superaromatic systems with a predominance of multicentre bonding. However, the electron count rules derived for such systems are applicable only to a limited range of skeletal compounds. In the next Section certain specific structures of metal clusters are considered in order to establish more definitely the limits of applicability of the qualitative theoretical structural schemes described above.

III. THE STRUCTURE OF TRANSITION METAL CLUSTERS

1. Trinuclear and Tetranuclear Clusters†

In these simplest polynuclear derivatives all the metal–metal bonds can be regarded as of the two-electron two-centre types; the magic numbers of the valence electrons of the

†The electronic structure of trinuclear metallocycles is examined in detail in S.P.Gubin's review (see this issue of the Journal).

cluster can therefore be determined in accordance with the EAN rule (Fig.1). The bonding and antibonding (in relation to the metal atoms) MO in these clusters are of course delocalised throughout the polyhedron, but they can be expressed mathematically by the combination of localised two-electron two-centre interactions. Many trinuclear and tetranuclear clusters of Group VI–VIII transition metals with carbanion π-olefin ligands obey the EAN rule (see, for example, Chini et al.[1] and Wade[2]).

However, in the present discussion we shall be interested in precisely those clusters which do not correspond to the commonest magic numbers and for this reason are more rarely dealt with in review communications. Certain representatives of the extremely numerous group of such compounds are compiled in Table 1, which also lists the principal characteristics of the cluster fragment in the molecule. Comparison of the M–M distances in the cluster and in the crystal lattice of the metal does not yield an unambiguous criterion for the existence (and even more so the multiplicity) of the metal–metal bond, although the sums of the Pauling metal atom radii are also listed in Table 1 to characterise the general trends in the variation of the interatomic distances.

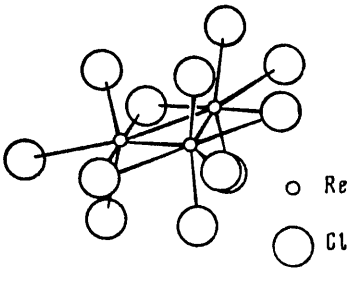


Figure 6. The structure of the $[Re_3(\mu_2\text{-}Cl)_3Cl_6]^{3-}$ cluster.[49]

Trinuclear and tetranuclear complexes of transition metals which do not obey the EAN rule can be arbitrarily divided into three non-equivalent groups. The first least numerous of these comprises clusters of the type $Os_3(CO)_{10}H_2$ in which the consequences of the deviation from the EAN rule can be readily interpreted within the framework of this same rule. Thus, the short Os–Os distance (2.680 Å) in $Os_3(CO)_{10}H_2$ can be attributed to a metal–metal double bond; multiplicities of 4/3 and 3/4 can be attributed to the Re–Re bonds (2.913 Å) in $Re_4(CO)_{12}H_4$ and the Ni–Ni bond (2.464 Å) in $Cp_4Ni_4H_3$ respectively; indeed, the average Re–Re distance (3.111 Å) in the 60-electron dianion $[Re_4(CO)_{12}H_6]^{2-}$ is greater by 0.20 Å than that observed in $Re_4(CO)_{12}H_4$.[47] The situation in the nickel derivative is somewhat more complex because the average Co–Co bond length in the 60-electron $Cp_4Co_4H_4$ cluster is 2.467 Å,[47] while the covalent radii of the cobalt and nickel atoms are similar; there exist also other nickel derivatives with an electron excess, for example, nickelocene, in which the presence of "superfluous" electrons does not lead to a structurally significant loosening of the bonds. The $Os_3(CO)_{10}H_2$ and $Re_4(CO)_{12}H_4$ clusters, which constitute an infrequent instance of the exception proving the rule, are regularly mentioned in theoretical studies.[2,23,25]

The trinuclear (Fig.6) complexes of Group II elements with halide and chalcogenide ligands of the type of $[Re_3Cl_{12}]^{3-}$ [49] or $[W_3O(OAc)_6(OH_2)_3]^{4+}$ [50] are discussed much more rarely in the literature devoted to the electronic structure of clusters. The number of valence electrons in these clusters (42ē) formally agrees with the existence of M=M double bonds, but such bonds in $[Re_3(\mu_2\text{-}Cl)_3Cl_3]^{3-}$ are shorter by 0.4 Å than the Re–Re bond in the dinuclear $H_2Re_2(CO)_8$ cluster (2.896 Å),[52] which can also be regarded as the double bond judging from the total number of electrons in the molecule. In terms of the "inorganic" (see above) electron counting scheme, the presence of double bonds has also been postulated in the trinuclear complexes considered.[49] Even more electron deficient clusters, for example $Re_3Cl_3(CH_2SiMe_3)_6$, in which the triangular $Re_3(\mu_2\text{-}Cl)_3$ fragment contains Re=Re double bonds 2.384–2.389 Å long according to the calculation based on the "inorganic" scheme, have been synthesised. However, according to the "organometallic" counting scheme, on the basis of the total number of valence electrons a multiplicity of 3 should be attributed to the same bonds. While it has certain advantages in the consideration of electronic structure, the existence of two electron counting schemes yielding inconsistent results nevertheless demonstrates that the description of the chemical bonds in clusters with halide and chalcogenide ligands has not been fully elaborated at the present time.

Table 1. Certain trinuclear and tetranuclear clusters not obeying the EAN rule.*

Formula	N_{val}	k_{M-M}	R (M–M), Å	R^M, Å	Refs.
$Os_3(CO)_{10}H_2$	46	3	2.81; 2.68	2.67	[44]
$Re_4(CO)_{12}H_4$	56	6	2.91	2.74	[45]
$Cp_4Ni_4H_3$	63	6	2.46	2.49	[46]
$[Re_3(\mu_2\text{-}Cl)_3Cl_6]^{3-}$	42	3	2.48	2.74	[49]
$[W_3(\mu_3\text{-}O)(\mu_2\text{-}OAc)_6(H_2O)_3]^{4+}$	42	3	2.75	2.74	[50]
$[Re_3Cl_3(CH_2SiMe_3)_6]$	36	3	2.39	2.74	[51]
$Pd_3(SO_2)_2[CN(t\text{-}Bu)]_5$	42	3	2.74	2.75	[53]
$Pt_3H_6[P(t\text{-}Bu)_3]_3$	42	3	2.82	2.77	[54]
$Pt_3[CN(t\text{-}Bu)]_6$	42	3	2.63	2.77	[55]
$Pt_3(CO)_3[P(C_6H_{11})_3]_4$	44	3	2.71	2.77	[56]
$Pd_3(CO)_3(PPh_3)_4$	44	3	2.72	2.75	[57]
$Pt_4H_2[P(t\text{-}Bu)_3]_4$	50	6	2.67; 2.80	2.77	[54]
$Pt_4H_6[P(iso\text{-}Pr)_2Ph]_4$	56	6	2.87; 3.08	2.77	[54]
$[Pd_4(phen)_4(CO)]^{2+}$	56	6	2.72; 2.89	2.75	[58]
$Pd_4(CO)_5(PPh_3)_4$	58	5	2.76	2.75	[57]
$Pt_4(CO)_5(PMe_2Ph)_4$	58	5	2.76	2.77	[59]
$Pd_4(CO)_6(PBu_3)_4$	60	6	2.78	2.75	[60]
$Cu_4(CH_2SiMe_3)_4$	48	4	2.42	2.55	[65]
$Cu_4(C_5H_4FeC_5H_5)_4$	48	4	2.44	2.55	[66]
$Ag_4(C_5H_4FeC_5H_5)_4$	48	4	2.74	2.88	[67]
$Cu_4[O(t\text{-}Bu)]_4$	56	0	2.71	2.55	[68]
$[Cu_4(SPh)_6]^{2-}$	64	0	2.76	2.55	[69]
$Cu_4(\mu_3\text{-}I)_4Py_4$	72	0	2.69	2.55	[70]
$[(C_5H_{11}N)AuCl]_4$	56	4	3.30	2.88	[71]
$Au_4(\mu_2\text{-}I)_2(PPh_3)_4$	58	6	2.74	2.88	[72]

*Notation: k_{M-M} is the number of metal–metal bonds in the cluster, R(M–M) the average metal–metal distance, and R^M the sum of the Pauling metal atom radii.[43]

The third and most varied group of "irregular" trinuclear and tetranuclear clusters consists of derivatives of pallidium, platinum, and copper subgroup metals. In contrast to the halide complexes, these clusters have recently attracted the attention of theoreticians,[23,33,35] but it would be premature at present to speak of the development of an electron counting scheme for such clusters. Certain analogues of magic numbers can be established empirically in palladium and platinum derivatives—they are usually smaller than in the corresponding complexes of the metals in the middle of the transition series, just as in the mononuclear derivatives of these elements the 16-electron shell is more stable than the 18-electron shell. Trinuclear 42- and 44-electron platinum and

palladium complexes, 56-electron tetrahedral clusters, and 58-electron clusters with the "butterfly" configuration are known (Table 1). The situation is complicated by the frequent deviations from these empirical magic numbers as well. Thus there exist the 50-electron tetrahedral $Pt_4.H_2[P(t\text{-}Bu)_3]_4$ and the 60-electron tetrahedral $Pd_4(CO)_6.[P(n\text{-}Bu)_3]_4$ clusters (the latter, included in Table 1, obeys the EAN rule in contradiction of the Table heading, which is more in the nature of an exception in the class of palladium and platinum derivatives). Assuming that the exopolyhedral Pt–Pt bonds in the pentanuclear $Pt_5(CO)_6(PPh_3)_4$ cluster (Fig.7) are two-electron two-centre bonds, we obtain yet another magic number—58ē for the Pt_4 tetrahedron.[61]

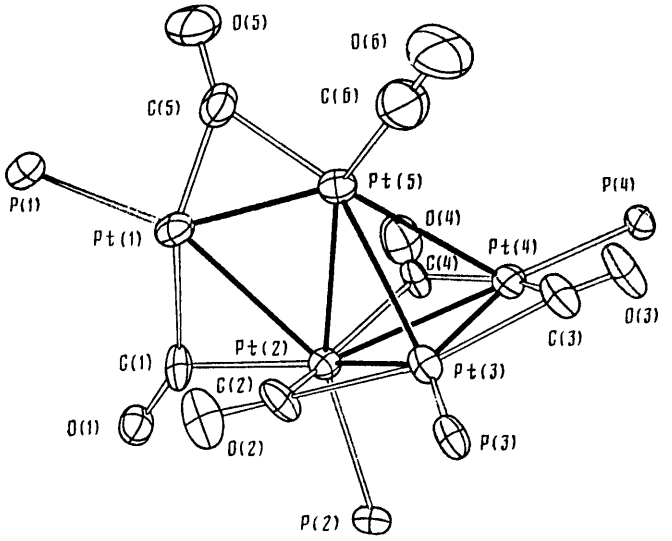


Figure 7. The $Pt_5(CO)_6(PPh_3)_4$ molecule (the phenyl substituents are not shown).[61]

The thermodynamically stable palladium and platinum clusters are able, in addition, to expand the coordination sphere of the metal atom, reacting under mild conditions with metallic mercury or its derivatives. Thus the bitetrahedral $\{[Ph(iso\text{-}Pr)_2P]_3Pt_3(CO)_3Hg\}_2$ cluster (Fig.8), which contains 54 or 53 electrons depending on whether the Hg...Hg contact 3.225 Å long is or is not regarded as a chemical bond,[62] the $[L_3Pt_3.(\mu_2\text{-}L)_3]_2Hg$ (where L = $Me_2C_6H_3NC$) *commo*-cluster of the sandwich type,[63] and the edge-condensed $Pd_4Hg_2Br_2(\mu_2\text{-}CO)_4.(PEt_3)_4$ cluster[64] have been obtained. Their electronic structure is difficult to interpret at the existing level of theoretical ideas.

The structures of the tetranuclear copper, silver, and gold complexes are even less susceptible to classification. The existence of the planar M_4 tetragon, which exhibits a tendency towards the formation of four additional M...Fe bonds in the ferrocenyl derivative $Cu_4(C_5H_4FeC_5H_4R)_4$ (R = $CH_2.NMe_2$) [66] (and in its silver analogue[67]), is characteristic of copper derivatives. The Cu–Cu distance in the 56-electron $Cu_4[O(t\text{-}Bu)]_4$ cluster (parallelogram) and in the 64-electron $[Cu_4(SPh)_6]^{2-}$ cluster (tetrahedron) is greater than in the formally 72-electron $Cu_4(\mu_3\text{-}I_4)Py_4$ complex, where metal–metal bonds should be absent according to the EAN rule. The Cu–Cu distances in the isoelectronic cubane-like clusters of the latter type vary in the range 2.65–3.21 Å.[70] The Cu–Cu contacts 2.6–2.8 Å long are not usually assumed to correspond to a direct metal–metal interaction.[68–70]

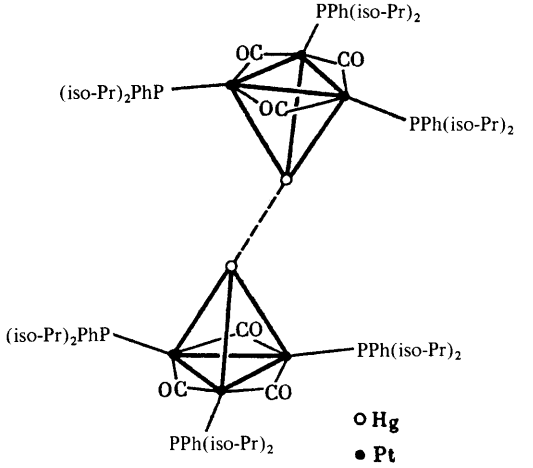


Figure 8. The $\{[Ph(iso\text{-}Pr)_2P]_3Pt_3(CO)_3Hg\}_2$ cluster (the hydrocarbon fragments are not shown).[62]

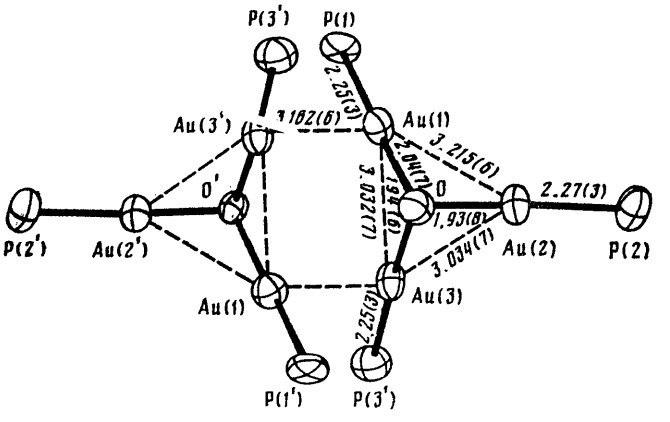


Figure 9. The structure of the $[(Ph_3PAu)_3O]_2^{2+}$ cation[74] (the phenyl substituents are not shown).

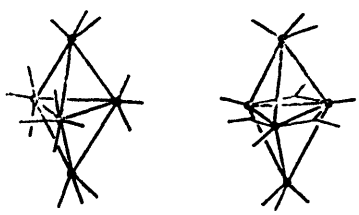
Somewhat in contrast to this, the gold derivatives definitely manifest a tendency towards a weak "secondary" Au...Au interaction at distances of 3.0–3.5 Å, which is observed, for example, in $C_5H_{10}NAuCl_4$.[71] The $Au_4(\mu_2\text{-}I)_2(PPh_3)_4$ structure contains the 58-electron Au_4 tetrahedron, while the formally 56-electron Au_4 tetrahedron in the pentanuclear $[Au_5(PPh_2.CH_2PPh_2)_3CH(PPh_2)_2]^{2+}$ dication is linked via one of its vertices to the 14-electron linearly coordinated Au atom.[73] Finally, two 42-electron $(LAu)_3E^+$ cations in the series of $[(LAu)_3E]_2^{2+}$ dimers (where L = PPh_3 and E = chalcogen atom[74,75]) are linked in pairs by secondary Au...Au interactions over distances of 3.15–3.40 Å (Fig.9).

We believe that the data examined suggest that the trinuclear and tetranuclear clusters of post-transition metals, palladium, and platinum do not on the whole exhibit an

unambiguous relation between the geometrical characteristics of the polyhedra present in their molecules and the numbers of valence electrons.

2. Trigonal-Bipyramidal Clusters

The trigonal-bipyramidal fragment is believed to be the first "Wade" *closo*-polyhedron and exists as such in the structures of a series of clusters satisfying the $2n + 2$ rule (Table 2, left half). According to this rule, clusters with 12 skeletal electrons, made up of the atoms of transition or non-transition elements are analogues of the *closo*-carbaborane $C_2B_3H_5$ (Fig.10). A characteristic feature of structures of the trigonal-bipyramidal type is, however, their intermediate position between polyhedra with localised and many-centre bonds, because the trigonal bipyramid can be equally well regarded as a one-cap tetrahedron, the localised bonding in which also requires twelve electrons. As a consequence of this, derivatives of the type $Os_4(CO)_{12}NMe$, for example, where the M_4 is a tetrahedron coordinated via a triangular face to the μ_3-NMe ligand, the M_4C or M_4N "butterfly" in which a non-metal atom is incorporated, or the M_3 triangle and two μ_3-X ligands, are sometimes classified as mixed trigonal-bipyramidal clusters.



a *b*

Figure 10. Examples of the "Wade" (*a*) and "non-Wade" (*b*) trigonal-bipyramidal clusters and the numbers of skeletal electrons in the latter: a) $Os_5(CO)_{16}$, $12\bar{e}$; *b*) $[Ni_5(CO)_{12}]^{2-}$, $16\bar{e}$.

This kind of borderline position of trigonal-bipyramidal structures is also expressed by the existence among them of a large number of exceptions to the $2n + 2$ rule (Table 2, right half) and these exceptions cannot at present be confidently ascribed to the presence in the polyhedron of the atoms of a post-transition element. The $[PtRh_4(CO)_{12}]^2$ ($12\bar{e}$) and $[PtRh_4(CO)_{14}]^{2-}$ ($16\bar{e}$) mixed clusters exhibit, for example, an isomeric behaviour of the cluster nucleus which depends on whether the Pt atom occupies the apical or equatorial position.

The characteristic features of the trigonal-bipyramidal complexes made it necessary to postulate the existence in them of two magic numbers (12 and 16) of skeletal electrons or (for clusters made up of transition metal atoms) of 72 and 76 valence electrons.[22,88] The experimentally observed increase in the length of the equatorial-apical metal–metal bonds compared with the equatorial-equatorial bonds in the 76-electron derivatives has been explained with the aid of EHM calculations.[22] However, Table 2 shows that there exist also clusters with ten and fourteen skeletal electrons. Among the polynuclear complexes of metals of the iron and cobalt subgroup trigonal bipyramidal derivatives are encountered much more rarely than the octahedral complexes.

3. Derivatives of Octahedral Clusters

The $2n + 2$ rule holds most rigorously for the octahedral clusters of transition metals of the iron and cobalt subgroups with carbonyl ligands, some of which can be substituted by other "soft" ligands (η^n-olefin, phosphine, and nitrosyl ligands). The examples in Table 3 show that the polyhedron in these clusters can consist of atoms of different elements [the heteronuclear $Ru_4C_2Me_2(CO)_{12}$ complex (Fig.11), in which the $Ru_4(CO)_{12}$ "butterfly" has been built onto the octahedron via the acetylene ligand of the complex bridging functional group is especially interesting[92]] or can incorporate a C or H atom within the cavity of the polyhedron. It is noteworthy that even the $Cp_6Ti_6O_8$ titanium cluster with μ_3-oxo-bridges and the heteronuclear carbide cluster $(Et_3PAu)_2.Fe_4C(CO)_{12}$ each have 14 skeletal electrons, differing in this respect from the majority of the polynuclear compounds at the beginning and end of the transition series which have been investigated. Pentanuclear *nido*- and *arachno*-derivatives which can be synthesised from octahedral clusters, are also known. Thus a 14-electron tetragonal pyramid can be obtained by removing one vertex of the octahedron (this leads to a general method of synthesis of heteronuclear clusters, as a result of the successive introduction of atoms of other transition elements in place of the missing vertex[94]), while a 16-electron *arachno*-cluster can be obtained by adding two-electron donors to the corresponding *nido*-derivatives (Fig.12).

Table 2. Examples of trigonal-bipyramidal clusters.†

Formula	N_{sk}	Refs.	Formula	N_{sk}	Refs.
$C_2B_2H_5$	12	[76]	$Ph_3PAuRu_3Co(CO)_{11}$	10	[83]
Sn_5^{2-}	12	[77]	$Cp_2Cr_2Co(\mu_3\text{-}S)_2[\mu_2\text{-}$	10	[84]
$Os_5(CO)_{16}$	12	[78]	$\text{-}S(t\text{-}Bu)](CO)_2$		
$[PtRh_4(CO)_{12}]^{2-}$	12	[79]	$Cp_5V_5O_6$	14	[85]
$Os_4(CO)_{12}(\mu_3\text{-}NMe)$	12	[80]	$Cp_3Co_3(\mu_3\text{-}S)_2$	14	[86]
$HRu_4N(CO)_{11}P(OMe)_3$	12	[81]	$[RuIr_4(CO)_{15}]^{2-}$	16	[79]
$[Ni_3S_2(PEt_3)_6]^{2+}$	12	[82]	$[Ni_5(CO)_{12}]^{2-}$	16	[87]
			$[PtRh_4(CO)_{14}]^{2-}$	16	[79]
			$Cp_3Ni_3(\mu_3\text{-}S)_2$	17	[88]

†N_{sk} is the number of skeletal electrons in the cluster.

Table 3. The "Wade" octahedral clusters of Group IV–VIII transition metals and their derivatives.

Formula	N_{val}	N_{sk}	R (M–M), Å	R^M, Å	Refs.
$Rh_6(CO)_{16}$	86	14	2.78	2.68	[13]
$[Co_6H(CO)_{15}]^-$	86	14	2.58	2.48	[89]
$Ru_6C(CO)_{14}(C_6H_3Me_3)$	86	14	2.88	2.65	[90]
$Cp_6Ti_6O_8$	86	14	2.89	2.98	[91]
$Ru_4C_2Me_2(CO)_{12}$	66	14	2.75	2.65	[92]
$(Et_3P)_2Au_2Fe_4C(CO)_{12}$	86	14	2.92 (Fe—Au) 2.65 (Fe—Fe) 3.02 (Au—Au)	2.88 (Au) 2.49 (Fe)	[93]
$HFe_3N(CO)_{14}$	74	14	2.58	2.49	[95]
$Ru_5C(CO)_{15}NCMe$	76	16	2.85	2.65	[96]
Cp_6Ni_6	90	18	2.42	2.49	[97]
$[Fe_6S_8(PEt_3)_6]^{2+}$	90	18	2.62	2.49	[98]

The cyclopentadienylnickel cluster Cp_6Ni_6 (its monocation is also known[97]) and the iron cluster[98] $Fe_6S_8(PEt_3)_6$ with phosphine and μ_3-sulphide ligands, in which there is a significant loosening of the metal–metal bonds, are exceptions to Wade's

rule. It is of interest to note that, in contrast to its analogues in the Periodic System, clusters with an electron excess are fairly characteristic of nickel, namely $Cp_4Ni_4H_3$,[46] $[Ni_5.(CO)_{12}]^{2-}$,[87] and Cp_6Ni_6.[97]

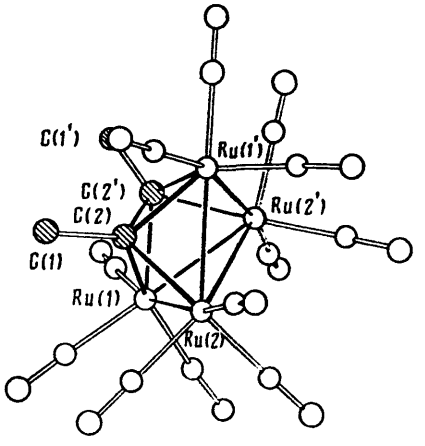


Figure 11. The structure of $Ru_4C_2Me_2(CO)_{12}$.[92]

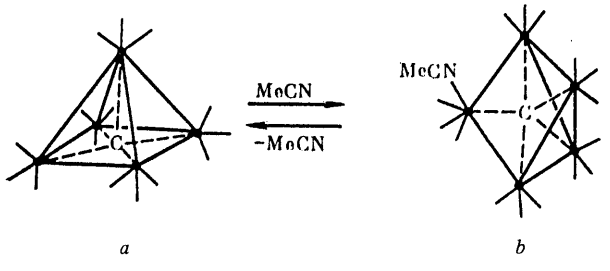


Figure 12. The interconversions of the *nido*- and *arachno*-clusters of ruthenium: *a*) $Ru_5C(CO)_{15}$, 14$\bar{e}$; *b*) $Ru_5C(CO)_{15}.(MeCN)$, 16$\bar{e}$.

Among octahedral clusters, there exist also numerous "non-Wade" derivatives, including, in particular, the halide complexes of Group III-VI transition metals (Table 4). The $M_6(\mu_2\text{-}X)_{12}$ and $M_6(\mu_3\text{-}X)_8$ motifs, where the halogen atoms form bridges along all the edges or along all the faces of the octahedron with additional apical coordination of the ligands to its vertices, occur widely in these clusters, which are distinguished by a fixed configuration of the ligand environment relative to the metallopolyhedron. The chemical bonds in the cluster nuclei of such compounds are usually described qualitatively in terms of the "inorganic" electron counting scheme which is not identical to the "organometallic" scheme adopted in this review.

Wade attempted to combine the two approaches[2] by postulating the involvement of four AO from each metal atom in skeletal bonding in "non-Wade" clusters. The bonds in the $[Nb_6(\mu_2\text{-}Cl)_{12}]^{2+}$ and $[Mo_6(\mu_3\text{-}Cl)_8]^{4+}$ model clusters are then assumed to be respectively two-electron three-centre bonds (eight bonds, 16$\bar{e}$) or two-electron two-centre bonds (twelve bonds, 24$\bar{e}$). Apart from the reduction of the predictive power of such a model as a consequence of the introduction of bonds with different degrees of localisation into isotypical compounds, one should note that the formal charge separation in the molecule by no means allows the isolation of the cluster fragments of the above types in all the existing octahedral metal complexes with halide ligands.

Table 4. Cluster transition metal halides.

Formula*	N_{val}	R (M—M), Å	R^M, Å	Refs.
$Zr_6(\mu_2\text{-}I)_{12}$	72	3.20	3.13	[99]
$[Nb_6(\mu_2\text{-}Cl)_{12}Cl_6]^{2-}$	74	3.02	2.85	[100]
$Nb_6(\mu_2\text{-}Cl)_{12}(Cl_{4/2})$	75	2.92	2.85	[101]
$[Ta_6(\mu_2\text{-}Cl)_{12}(CN)_6]^{4-}$	76	2.93	2.85	[102]
$W_6(\mu_2\text{-}Cl)_{12}Cl_6$	78	2.92	2.74	[103]
$[Nb_6(\mu_3\text{-}I)_8(I_{6/2})]^-$	80	2.83	2.85	[104]
$Mo_6(\mu_3\text{-}Cl)_8Br_6]^{2-}$	84	2.62	2.72	[105]

*The fractional subscripts correspond to compounds in the crystals of which the vertices of two neighbouring clusters are linked by bridging halide ligands.

The evaluation of the number of valence electrons in the metallopolyhedra of the compounds listed in Table 4 suggests that a characteristic feature of these polynuclear complexes is the absence of magic numbers as such rather than the existence of magic numbers (they could be found empirically from the available experimental data) other than in the carbonyl clusters. We believe that the reason for this may lie in the "super-electron deficiency" of the cluster derivatives of metals at the beginning of the transition series as a result of which the corresponding metallopolyhedron is coordination-saturated even before its ability to receive the electrons supplied by the ligand has been exhausted, i.e. before all its low-energy CVMO have been occupied. It is noteworthy that the $Cp_6Ti_6O_8$ cluster with many-electron ligands satisfies the $2n + 2$ rule.[91]

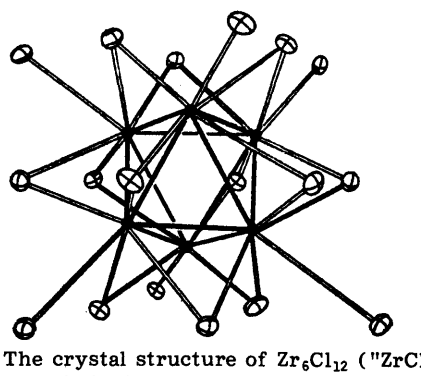


Figure 13. The crystal structure of Zr_6Cl_{12} ("$ZrCl_2$"). The metallopolyhedron is indicated; the Cl atoms in the equatorial belt are coordinated to the vertices of neighbouring octahedral clusters.

Yet another feature of the cluster transition metal halides is the breakdown of the principle of the uniform occupation of the coordination sphere of the metallopolyhedron by ligands,

which is valid for the corresponding carbonyl analogues.[6] Thus an arrangement of Cl ligands in layers is observed (Fig.13) in the Zr_6Cl_{12} structure, while the μ_2-Cl ligands in the equatorial component of the coordination shell are additionally coordinated along the vertices of neighbouring octahedra. The structural motifs examined are also common in organic clusters with chalcogenide ligands (Chevrel phases); metallo-octahedra with a mixed halide-chalcogenide environment are also known.

Derivatives of post-transition metals constitute yet another group of non-Wade octahedral clusters by analogy with the trinuclear and tetranuclear structures which do not obey the EAN rule. Few structural studies have so far been made on polynuclear compounds of this class, where (Table 5) the absence of magic numbers rather than an appreciable preference for particular electronic configurations is to be seen in the cluster halides of metals at the beginning of the transition series. The ammine, phosphine, and σ-aryl (more rarely σ-alkyl) groups are characteristic ligands for the elements of the copper subgroup.

Table 5. Hexanuclear clusters of post-transition elements.

Formula	N_{val}	N_{sk}	R (M–M), Å	r^M, Å	Refs.
$Ir_2Cu_4(\sigma,\pi\text{-}C{\equiv}CPh)_8(PPh_3)_2$	90	18	2.74 (Cu—Cu) 2.87 (Cu—Ir)	2.52 (Cu) 2.71 (Ir)	[106]
$H_6Cu_6(PPh_3)_6$	84	12	2.60	2.55	[107]
$Cu_6(o\text{-}Me_2NC_6H_4)_4(\mu_2\text{-}Br)_2$	84	12	2.61	2.55	[108]
$Cu_4(o\text{-}Me_2NC_6H_4)_4(\mu\text{-}C_2Ph)_2$	80	8	2.58	2.55	[109]
$[Ag_6[S_2C{=}C(CN)_2]_6]^{6-}$	96	24	3.04	2.88	[110]
$[Au_6(PTol_3)_6]^{2+}$	76	4	3.02	2.88	[30]
$Au_6(PPh_3)_4[Co(CO)_4]_2$*	76	4	2.75	2.88	[111]
$[(Ph_3P)_2Au_3(\mu_3\text{-}O)]_2^{2+}$	84	12	3.11	2.88	[74]

*The $Co(CO)_4$ fragments play the role of ligands, forming exopolyhedral Au–Co bonds.

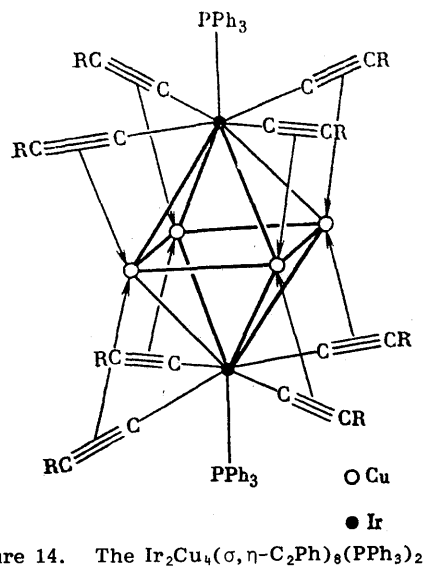


Figure 14. The $Ir_2Cu_4(\sigma,\eta\text{-}C_2Ph)_8(PPh_3)_2$ cluster.

Thus the $Ir_2Cu_4(C_2Ph)_8(PPh_3)_2$ cluster (Fig.14) contains 18 skeletal electrons, if each σ,π-acetylide is regarded as the donor of five electrons, or proves to be super-electron-deficient if it is assumed that these ligands each supply three electrons (this is more usual in the case of one-centre π-coordination of alkynes). The task of explaining the existence, inconsistent with calculated data, of the octahedral $[Au_6(PTol_3)_6]^{2+}$ (Tol = *p*-tolyl) cluster and the isoelectronic bitetrahedral $Au_6(PPh_3)_4[Co(CO)_4]_2$ cluster is made still more difficult by the presence of a bitetrahedral configuration, analogous to that in the latter cluster, in the 82-electron polyhedron (discussed above) in $Pd_2Hg_2Br_2(CO)_4(PEt_3)_4$. On the other hand, dications of the type $[(Ph_3PAu)_3E]_2^{2+}$ (E = S, Se, or Te—see Fig.9), which are isoelectronic with the octahedral copper clusters $H_6Cu_6(PPh_3)_6$ and $Cu_6(o\text{-}Me_2NC_6H_4)_4(\mu_2\text{-}Br)_2$, contain an open tricyclic Au_6 skeleton. Finally, distorted Ag_6 octahedra with Ag...Ag contacts 3.01 and 3.74 Å long, which are a general characteristic of polynuclear silver compounds normally containing complex polyatomic skeletons, are present in the $\{Ag_6[S_2C{=}C(CN)_2]_6\}^{6-}$ structure.[110]

Table 6. Clusters of medium size.

Formula	Reference polyhedron	No. of caps	N_{val}	N^{val}_{CVMO}	N_{sk}	$N^{sk}_{(2n+2)}$	Refs.
$[Rh_7(CO)_{16}]^{3-}$	Octahedron	1	98	98	14	14	[112]
$[Os_8(CO)_{22}]^{2-}$	"	2	110	110	14	14	[113]
$[Re_8C(CO)_{24}]^{2-}$	"	2	110	110	14	14	[114]
$[Os_{10}C(CO)_{24}]^{2-}$	"	4	134	140	14	14	[29]
$Pd_7(CO)_7(PMe_3)_7$	"	1	98	98	14	14	[116]
$Pd_{10}(CO)_{12}[P(n\text{-}Bu)_3]_6$	"	4	136	140	16	14	[60]
$Hg_6Rh_6(PMe_3)_6$	"	4	132	140	12	14	[117]
$[Pd_6Fe_6(CO)_{24}H]^{3-}$	"	6	160	166	16	14	[118]
$[Rh_9(CO)_{19}]^{3-}$	Two octahedra with common face	0	122	124	14	14	[121]
$[Ru_{10}(C)_2(CO)_{24}]^{2-}$	Two octahedra with common edge	0	138	130	18	18	[122]
$[Rh_{11}(CO)_{23}]^{3-}$	Three octahedra with common faces	0	148	—	16	14	[124]
$[Rh_9P(CO)_{21}F]^{-}$	Tetragonal antiprism	1	130	130	22	22	[125]
$[Rh_{16}S(CO)_{22}]^{2-}$	Ditto	2	142	142	22	22	[127]
$[Sn_9Tl]^{3-}$	"	2	42	—	22	22	[128]
$[Co_8(CO)_{18}C]^{2-}$	"	0	114	114	18	22	[129]
$[PtRh_{10}N(CO)_{22}]^{3-}$	Trigonal prism	5	150	146	18	20	[132]
$[Bi_9]^{5+}$	Ditto	3	40	—	22	20	[133]
$[Rh_{12}Sb(CO)_{27}]^{3-}$	Eicosahedron	0	170	170	26	26	[135]

Notation: N_{val} is the number of valence electrons in the cluster, N^{val}_{CVMO} the number of valence electrons calculated in accordance with Lauher's scheme, N_{sk} the number of skeletal electrons in the cluster, and $N^{sk}_{(2n+2)}$ the number of skeletal electrons predicted by Wade's rule.

Evaluation of the number of skeletal electrons in fairly representative groups of clusters with an octahedral structure based on different transition and post-transition elements thus demonstrates a consistent character of the electronic structure in derivatives of metals in the middle of transition series and the apparent absence of such regularities in clusters of the elements at the beginning and end of the transition series. The causes of the failure of the magic number (2*n* + 2) rule for elements to the left and right of Fe and Co as well as their analogues are evidently various, but we believe that the very fact of such behaviour of metal clusters reveals a close relation between the 2*n* + 2 and EAN rules, because the regions of their applicability in the series of transition elements are virtually identical.

4. Clusters Based on Polyhedra of Medium Dimensions

Metal clusters containing M_n polyhedra with a number of vertices n between 7 and 12 will be assigned to this group of polynuclear compounds. Most of such clusters consist of osmium and rhodium derivatives; cobalt, palladium, and gold compounds have also been investigated. Table 6 presents examples of such clusters; the numbers of their valence electrons are compared with the numbers found in accordance with the $2n + 2$ rule and calculated on the basis of the CVMO scheme.[22-24] Among the compounds considered, it is possible to differentiate several types of structures differing in the "reference" polyhedra which can have one or several caps. We shall consider subsequently the polyhedra of each type in order of increasing complexity of their reference polyhedron.

(a) Octahedra with centred faces. Clusters of this type have no analogies in the structures of boranes and carbaboranes. According to the $2n + 2$ scheme, the addition of a cap (i.e. a vertex over the centre of a triangular face) to an octahedral cluster does not increase the number of skeletal electrons of the octahedron. Accordingly, in the known clusters of metal-analogues, namely manganese, iron, and cobalt, having the structures of one-, two-, and four-cap octahedra, the magic number of skeletal electrons $N_{sk} = 14$ obtains. The electronic structure of the ten-vertex cluster $[Os_{10}C(CO)_{24}]^{2-}$,[29] which cannot be interpreted within the framework of the CVMO scheme on the basis of the results of EHM calculations, is in reality rigorously consistent with Wade's rule, which has been confirmed in a series of recent studies on derivatives of clusters of this type.[115]

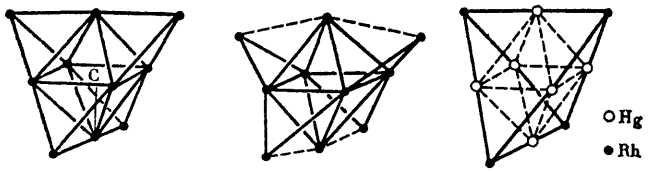


Figure 15. Decagonal clusters with a four-cap octahedron made up of metal atoms and the numbers of skeletal electrons in them: *a*) $[Os_{10}C(CO)_{24}]^{2-}$, 14ē;[29] *b*) $Pd_{10}(CO)_{12}(PBu_3)_6$, 16ē;[60] *c*) $Hg_6Rh_4(PMe_3)_{12}$, 12ē.[117]

Deviations from Wade's rule appear in the analogous palladium derivatives: the observed "opening of caps" requires the appearance of additional electrons relative to the closed electronic configuration, namely two in $Pd_7(CO)_7(PMe_3)_7$ and eight in $Pd_{10}(CO)_{12}[P(n\text{-}Bu)_3]_6$, which is inconsistent with the real numbers of valence electrons in these clusters. The number $N_{val} = 160$ in the dodecanuclear cluster $[Pd_6Fe_6.(CO)_{24}H]^{3-}$ [118] corresponds to $N_{sk} = 16$, which is inconsistent with the $2n + 2$ rule, but can be reproduced in terms of the CVMO scheme; at present it is not entirely clear whether the observed distortions of the trigonal-antiprismatic type in the internal Pd_6 octahedron are a result of the deviation from Wade's magic number $N_{sk} = 14$. For the $Hg_6Rh_4.(PMe_3)_{12}$ cluster, the establishment of a correlation between the number of electrons and the geometrical characteristics of the polyhedra constitutes a still more difficult task. Examples of decanuclear clusters (Fig.15) illustrate yet again the loss of predictive power by Wade's rule for clusters of metals at the end of the transition series.

(b) Polyoctahedral clusters. The $2n + 2$ rule can apparently be extended (provided that it is valid for the constituent polyhedra) to clusters consisting of two or several polyhedra having common vertices (*commo*-clusters, polyhedra with a common edge and a common face); by relating the number of skeletal electrons in such compounds to the number of non-common vertices, i.e. vertices which do not belong simultaneously to two or several polyhedra. Accordingly, the numbers of skeletal electrons in the recently synthesised $[Rh_9(CO)_{19}]^{3-}$ and $[Ru_{10}(C)_2(CO)_{24}]^{2-}$ clusters and also in the mixed cluster $Os_6C(CO)_{16}(C_2Me_2)$ [121] are analogous to those required for the corresponding *closo*-hexagon, *closo*-octagon, and *arachno*-hexagon (Fig.16).

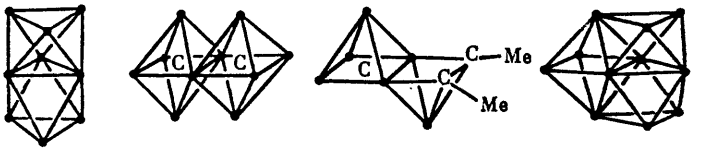


Figure 16. Polyoctahedral clusters and the numbers of skeletal electrons observed in them: *a*) $[Rh_9(CO)_{15}]^{3-}$, 14ē;[121] *b*) $[Ru_{10}(C)_2(CO)_{24}]^{2-}$, 18e;[122] *c*) $Os_6C(CO)_{16}C_2Me_2$, 18ē;[123] *d*) $[Rh_{11}(CO)_{23}]^{3-}$, 16ē.[124]

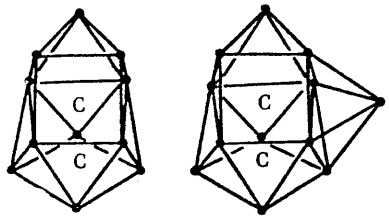
A more general rule for the calculation of the magic numbers of valence electrons for any multipolyhedral clusters has now been proposed by Mingos;[120] the total magic number of valence electrons of the cluster is equal to the sum of the magic numbers of its constituent polyhedra minus the sum of the magic numbers of the boundary fragments (18ē for a single atom in *commo*-clusters, 34ē for two atoms located on a common edge of the cluster, and 48ē for three atoms on a common triangular face or 50ē for a common face in polyhedra with electron delocalisation). Mingos's rule makes it possible, for example, to obtain the magic number of valence electrons in a trigonal bipyramid regarded as two tetrahedra with a common fact (60 + 60 − 48 = 72ē) and is valid for a large number of clusters of a wide variety of types.# We may recall that the numbers of valence and skeletal electrons in the cluster differ by $12n$, where n is the number of atoms in the cluster.

It is noteworthy that Wade's magic numbers characterise a trend rather than a rigorous rule in the geometrical structures of clusters in the case of compound polyhedra: thus the distances between the apical atoms of the two octahedra in $Ru_{10}(C)_2(CO)_{24}]^{2-}$ not linked by valence forces (Ru...Ru contacts 3.112 and 3.138 Å long) exceed only slightly the

#Analogous rules have been proposed in a recent study by Mingos and Evans[148] for platinum clusters. In this case the magic numbers of boundary fragments are 16ē for a common vertex, 30ē for a common edge, and 44ē for a common triangular face. For the pentanuclear cluster $Pt_5(CO)_6(PPh_3)_4$, the scheme predicts the number 70ē, which agrees with the true number (see, however, Section III, 2 of the present review).

lengths of certain edges (2.803–3.098 Å). However, the CVMO scheme yields for these clusters numbers of valence electrons which are inconsistent with the observed numbers.[24] The trisoctahedral cluster having the composition $[Rh_{11}(CO)_{23}]^{3-}$ indicated in Table 6 deviates from the $2n + 2$ rule; calculations of its electronic structure on the basis of the CVMO scheme have not been carried out. The presence of five long edges (2.96–3.06 Å) in the Rh_{11} polyhedron has been rationally explained [124] by the deformation of its constituent condensed octahedra, because in this case octahedra do not fill the three-dimensional space.

(c) Clusters based on a tetragonal (Archimedes) antiprism. The recently synthesised derivatives of this type with one (*nido*-M_9) or two (*closo*-M_{10}) caps over the "open" tetragonal faces of the reference polyhedron contain 22 skeletal electrons in conformity with the $2n + 2$ rule. The inner cavity of the rhodium clusters contains P, S, or As atoms. It is of interest that the specific metal–metal distances in this group of clusters can vary within fairly wide limits (particularly in the polyhedral anions Sn_8Tl^{3-} and Sn_9Tl^{3-}).[128] In essence, on the basis of the $2n + 2$ rule, it is possible to predict in compounds of the given type only an idealised configuration of the polyhedron, which in the real structure may undergo considerable distortions. It is noteworthy that in the carbaborane derivatives of analogous structure the $2n + 2$ rule holds extremely rigorously.[2]



a *b*

Figure 17. *a*) $[Co_{11}C_2(CO_{22})]^{3-}$; *b*) $Rh_{12}C_2(CO)_{25}$.

(d) Polyhedra with an irregular structure. We understand this term to mean metal clusters of complex form in the structures of which it is possible to isolate the reference polyhedron only tentatively. Such compounds are usually characterised by fairly significant deviations from the $2n + 2$ rule. The $[Co_8C(CO)_{18}]^{2-}$ cluster occupies an intermediate position between those examined in the present and previous Sections: it has a tetragonal antiprismatic type of structure, but, as a consequence of distortion, it is also close to a two-cap trigonal prism (one of the open faces of the antiprism is "pierced" by the Co...Co contact 3.225 Å long); the number of skeletal electrons in this cluster does not agree with Wade's rule (but is correctly reproduced in terms of the CVMO scheme[22]). The distortions of the polyhedron considered have been explained[1] as a result of the discrepancy between the covalent radius of the carbon atom (0.77 Å) and the somewhat larger internal cavity in clusters of the tetragonal-antiprismatic type (capable of incorporating the atoms of non-metals in the Third and Fourth Period, as can be seen from the previous Section).

The undecanuclear $[Co_{11}C_2(CO)_{22}]^{3-}$ cluster[130] and the dodecanuclear $Rh_{12}C_2(CO)_{25}$ cluster[131] (Fig.17), containing in the inner cavities the diatomic C_2 group with C–C distances of 1.62 and 1.48 Å respectively, are even less susceptible to an "idealised" description. In the complex polyhedra of these clusters, each of which has two open tetragonal faces, there are 22 skeletal electrons in each case, i.e. the number N_{sk} characteristic of a *closo*-decagon holds. The presence of open faces thus ceases to affect the total number of skeletal electrons, which also remain unchanged following the appearance of a cap over each face.

The heteronuclear nitride cluster $[PtRh_{10}N(CO)_{21}]^{3-}$ can be represented by a three-cap trigonal prism with two additional caps, each of which constitutes simultaneously the centre of two rectangular faces; however, the lateral edges of such a prism are lengthened up to "non-bonding" Rh...Rh distances and amount to ~3.50 Å (Fig.18). The super-electron-deficient metalloborane and metallocarbaborane clusters have an analogous structure (see Yanovskii's review in this Journal).

Distortions of the type indicated are a general characteristic of trigonal-prismatic clusters with caps, which can be illustrated by the structure of Bi_9^{5+}.[133] In this polynuclear cation the lateral edges of the reference prism have been lengthened to 3.704–3.979 Å, while the other Bi–Bi distances in the polyhedron are in the range 3.078–3.286 Å. The number of electrons in Bi_9^{5+} is greater than the Wade number by 2, which is consistent with the predictions of the CVMO scheme for rhodium clusters.[22]

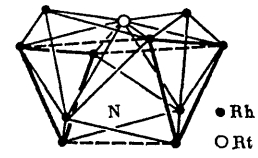


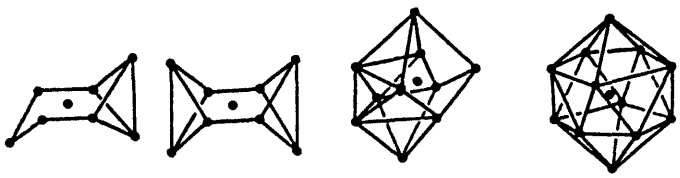
Figure 18. The $[PtRh_{10}N(CO)_{21}]^{3-}$ cluster[132] (the reference polyhedron is indicated).

(e) Clusters based on a centred eicosahedron. Among carbaboranes and metallo-carbaboranes, eicosahedral derivatives constitute the largest class which is most consistent with the $2n + 2$ rule.[134] On the other hand, with increase of the size of the polyhedron in metal clusters a tendency arises towards the breakdown of this rule. In the single structurally investigated distorted eicosahedral rhodium cluster $[Rh_{12}Sb(CO)_{27}]^{3-}$ the inner cavity is occupied by an Sb atom (the Sb–Rh distances are 2.712 and 2.922 Å) and, for the average Rh–Rh bonding distance in the polyhedron of 2.912 Å, three edges of the cluster are extended to 3.334 Å.[135] Despite the existence of "semiopen" faces, the cluster contains 26 skeletal electrons, which is typical for a *closo*-eicosahedron. The closeness of the covalent radii of the Sb (1.36 Å) and Rh (1.32 Å) atoms[43] is responsible for the possibility of the existence of homoatomic centred polyhedra. Indeed, long before the synthesis of $[Rh_{12}Sb(CO)_{27}]^{3-}$ its isoelectronic derivatives $[Rh_{13}(CO)_{24}H_n]^{(5-n)-}$ were obtained.[1] Their structures will be examined in the next Section (in view of their close relationship with the large carbonyl clusters).

Yet another extremely interesting class of polynuclear complexes, constructed in accordance with the eicosahedral motif, is known, namely the gold clusters (Fig.19). The oldest representative of this series, the $[Au_{13}(PMe_2Ph)_{10}Cl_2]^{3+}$ cluster,[32] was initially predicted by Mingos on the basis of EHM calculations.[31] The clusters whose structures have been

investigated so far and whose polyhedra can be represented by an eicosahedron with different numbers of missing vertices are compiled in Table 7 (L is a phosphine ligand). §

Table 7 shows that, in contrast to the gold derivatives examined previously, clusters of this type exhibit a definite tendency towards the retention of the magic number N_{sk} = 18, which is inconsistent with the number N_{sk} = 26 required for the eicosahedron according to the $2n + 2$ rule. For $[Au_8PPh_3)_8]^{2+}$, this is achieved by virtue of the weak coordination of one of the Ph_3P ligands to the central Au atom.[136]



a *b* *c* *d*

Figure 19. Centred gold clusters: *a*) $Au_8L_7^{2+}$; *b*) $Au_9L_8^{3+}$; *c*) $Au_{11}L_{10}^{3+}$; *d*) $Au_{13}L_{10}Cl_2^{3+}$.

On the basis of the preferential contribution of the interaction between the central and peripheral Au atoms to the bonding in the given cluster (this has been established both by calculations[131] and experimentally[139]), one can assume that the magic number N_{sk} = 18 characterises the tendency of the electron shell of the central Au atom in compounds of this type to assume the inert gas configuration.

Table 7. Centred gold clusters based on the eicosahedron.*

Formula	n_{miss}	N_{val}	N_{sk}	Refs.
$[Au_8L_7]^{2+}$	5	100	16	[136]
$[Au_8L_8]^{2+}$	5	102	18	[136]
$[Au_9L_8]^{3+}$	4	112	16	[137]
$[Au_{11}L_{10}]^{3+}$	2	138	18	[138]
$[Au_{13}L_{10}Cl_2]^{3+}$	0	162	18	[32]

*n_{miss} is the number of missing vertices.

In contrast to the mononuclear Au complexes, where a linear configuration and a 14-electron shell are characteristic of many of such compounds, the peripheral Au atoms in the clusters listed in Table 7 occupy fairly uniformly the coordination shell of the central atom, which apparently constitutes a condition for the fulfilment of the EAN rule in mononuclear transition metal complexes. This makes it possible to expect the existence of the clusters, not as yet obtained, $[Au_{10}L_9]^{2+}$ and $[Au_{12}L_{11}]^{4+}$ (or their isoelectronic derivatives involving the substitution of some of the phosphine ligands by halide ligands, which reduces the overall positive charge) and possibly cations of the type $[Au_{14}L_{11}X_2]^{4+}$ or $[Au_{14}L_{10}X_3]^{3+}$ (where X = halogen) with an 18-electron configuration of the central Au atom in all such hypothetical structures. In the case of the 16-electron clusters $Au_9L_8^{3+}$ the somewhat more open flattened Au_9 skeleton (Fig. 19b) is apparently capable of rearranging to a structure with a centred crown.[140]

5. Lattice Clusters

Here we denote by this term polynuclear transition metal anions, predominantly those of Rh and Pt, where the M_n polyhedron actually represent a fragment of the crystal lattice of the metal. Clusters of the type $[Os_{10}C(CO)_{24}]^{2-}$ or $[Pd_6Fe_6(CO)_{24}H]^{3-}$ (Table 6), which have already been examined, may be assumed to contain layers of metal atoms, with hexagonal close packing, but it is still possible to interpret their electronic structure rationally in terms of a model of the reference octahedron with electron delocalisation over which caps with localised bonds have been constructed. In contrast to this, the examples of large clusters with carbonyl ligands listed in Table 8 cannot be arranged systematically on the basis of the $2n + 2$ rule and even less so the EAN rule. For some of these, the real numbers of valence electrons can be found by means of the CVMO scheme, but, generally speaking, precisely in this class of polynuclear compounds the above scheme starts to become inadequate for the task formulated (see Section II). Comparison of the theoretical magic numbers of valence electrons with the numbers for specific structures is complicated in this instance also by the difficulty of detecting carbonyl (and even more so hydride) ligands in the X-ray diffraction study of large clusters owing to the high scattering capacity of the metal atoms and the intense absorption, as a result of which, for example, the number of CO ligands in the last cluster in Table 8, namely $[Pt_{38}(CO)_{44}]^{2-}$, was established only tentatively

Table 8. Certain Rh and Pt lattice clusters.

Formula	n_{int}	n_{cap}	n_o	N_{val}	N_{sk}	$N^{sk}_{(2n+2)}$	N^{val}_{CVMO}	Refs.
$[Rh_{13}H_3(CO)_{24}]^{2-}$	1	0	6	170	26	38	170	[141]
$[Rh_{14}H(CO)_{25}]^{3-}$	1	1	5	180	24	38	182	[142]
$[Rh_{15}(CO)_{27}]^{3-}$	1	2	4	192	24	38	194	[143]
$[Rh_{15}(CO)_{30}]^{3-}$	1	2	4	198	30	38	—	[144]
$[Rh_{17}(CO)_{30}]^{3-}$	1	4	2	216	24	38	—	[145]
$[Rh_{22}(CO)_{37}]^{4-}$	1	6+3	0	276	24	38	280	[4]
$[Rh_{22}(CO)_{35}H_x]^{5-}$	2	8	2	$273 + x$	$33 + x$	46	—	[146]
$[Pt_{19}(CO)_{22}]^{4-}$	2	0	10	238	34	56	—	[147]
$[Pt_{26}(CO)_{32}]^{2-}$	3	0	6	326	50	60	—	[4]
$[Pt_{38}(CO)_{44}]^{2-}$	6	0	6	470	86	78	—	[4]

Notation: n_{int} is the number of internal atoms, n_{cp} the number of caps, n_o the number of open faces; for the significance of the remaining notation, see previous tables.

In relation to quantitative theoretical schemes, the lattice clusters in general exhibit fully the tendency already mentioned above for polyhedra of medium dimensions: with increase of the size of the polyhedron, its idealised form, consistent with the $2n + 2$ rule, is found to be capable of undergoing increasing distortions, which do not alter the number of valence (or skeletal) electrons. Accordingly, the

§A preliminary communication[149] concerning the synthesis and structural study of the mixed $[(Ph_3P)_{12}Au_{13}Ag_{12}(\mu\text{-}Cl_6]^{m+}$ cluster, constructed from three interpenetrating eicosahedra and containing three intrapolyhedral Au atoms, has been published.

$[Rh_{13}(CO)_{24}H_3]^{2-}$ cluster, which can be obtained from a cubo-octahedron by rotating by 180° one of the triangular faces (to reproduce the so-called "twin of the cubo-octahedron"), is isoelectronic with a *closo*-eicosahedron, despite the presence of six open faces, which formally require additional twelve skeletal electrons.

Analysis of structures with Rh_{14}–Rh_{17} polyhedra (Fig. 20), which arise after the addition of caps to the initial Rh_{13} cluster, shows that in the case of large carbonyl clusters there is in essence no difference between the triangular and non-triangular faces as regards the influence on the number of skeletal electrons of the polyhedron. However, these numbers are not predicted by any of the existing theoretical schemes and can apparently be different for polyhedra of isotypical structure. Thus a satisfactory theoretical scheme for large transition metal clusters with carbonyl ligands has not as yet been developed.¶

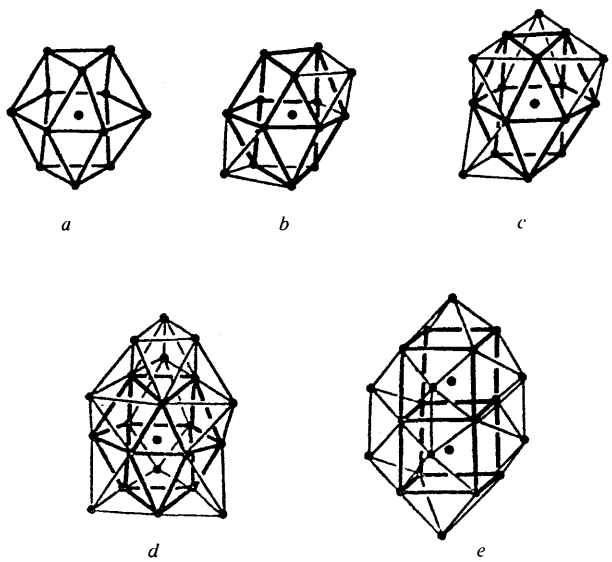


Figure 20. Examples of the structures of large metal clusters (the reference centred polyhedron is indicated): *a*) $[Rh_{13}.H_3(CO)_{24}]^{2-}$; *b*) $[Rh_{15}(CO)_{27}]^{3-}$; *c*) $[Rh_{17}(CO)_{30}]^{3-}$; *d*) $[Rh_{22}(CO)_{37}]^{4-}$; *e*) $[Rh_{22}(CO)_{35}H_x]^{5-}$.

- - - o 0 o - - -

On the basis of the structures of transition metal clusters examined above, it is possible to outline the limits of applicability of the existing schemes for the evaluation of the number of electrons in polyhedra. It follows from the examples in Section II that the "ordered region" in polynuclear transition metal complexes occurs in general in the vicinity of elements in the middle of transition series (Group VI–VIII metals), for "soft" ligands (in the first place CO), and for relatively simple M_n polyhedra with the number of vertices n in the range from 3 to 12. The $2n + 2$ rule or the EAN rule closely related to it (representing the special case for clusters with vertices of order ≤ 3 in which localised bonds can exist) yields the best results for such clusters.

The application of the $2n + 2$ scheme to octahedral metal clusters appears to be the most correct; an increase in the dimensions of the metallopolyhedron leads to increasing deviations of the structures of the clusters from the Wade structures and the corresponding magic numbers (somewhat in contrast to carbaborane derivatives, where eicosahedral clusters approximate most closely to the Wade structures).

The empirical-computational CVMO scheme which in general reproduces satisfactorily the numbers of valence electrons in clusters in the region of applicability of the $2n + 2$ rule, provides a somewhat better description of the electronic structure of clusters of medium dimensions, which sometimes deviates from this rule, and extends a little further into the region of large clusters; however, for a series of Wade polyhedra, this scheme can predict magic numbers which are incorrect. The search for general regularities outside the limits of the range of compounds indicated above and differentiated empirically has not so far achieved notable advances. Because of this, the hypothesis that clusters whose atomic and geometrical structures are governed by the $2n + 2$ rule contain a special type of chemical bond, which is absent from other clusters and which is taken into account explicitly or implicitly by electron counting schemes, appears to be fairly logical. According to all the theoretical and experimental studies, the chemical bond of this type in Wade clusters (and only in such clusters) makes it possible to differentiate independent topologically different exopolyhedral, surface, and intrapolyhedral electron systems with full localisation of electrons in the last two systems, which constitute overall the skeletal system of linkages in the clusters.[40] Thus Wade clusters (and only such clusters) apparently possess a closed configuration with skeletal delocalisation of the electron system, i.e. have the property of "three-dimensional" superaromaticity, which is nowadays attributed, not always with prejustification, to any polyhedral molecule.

In the superaromatic molecules, the bonding intrapolyhedral electron system ensures the stability of the cluster skeleton and the surface system ensures the electron delocalisation. The manifestation of superaromaticity in real cluster complexes, like the manifestation of the usual aromaticity in cyclic organic molecules, requires the fulfilment of specific geometrical conditions, which apparently follow from the requirement for the overlap of orbitals in the intrapolyhedral electron system. An increase in the size of the inner cavity, the appearance of open faces, or the introduction of atoms of post-transition elements into the polyhedral skeleton lead to a gradual loss of the property of superaromaticity and a transition to structures of clusters which do not obey the $2n + 2$ rule.

Comparison of structural data with theoretical predictions thus makes it possible to differentiate among the set of polynuclear compounds the region of clusters for which the model of chemical bonding in a superaromatic three-dimensional system developed at the present time is valid. However, at the present level of chemical theory, the model itself is mainly empirical in character and has not been rigorously justified mathematically. The search for such mathematical justification should apparently be prosecuted in the field of topology;

¶A dependence of the type of packing of the atoms in the metallopolyhedron on the average number of valence electrons per intrapolyhedral metal atom has been proposed recently for clusters of this type on the basis of a modified Hume–Rothery rule.[150] The total numbers of valence electrons in the clusters investigated, calculated on the basis of idealised types of packing, agree with the real numbers to within 4% (the discrepancies are in the range from 0 to 13 valence electrons).

the results of such investigations (should they be successful) might introduce a significant modification into the theoretical apparatus of the chemistry of cluster compounds.

REFERENCES

1. P.Chini, G.Longoni, and V.G.Albano, Adv.Organometal.Chem., 1976, **14**, 285.
2. K.Wade, Adv.Inorg.Chem.Radiochem., 1976, **18**, 1; in "Transition Metal Clusters" (Edited by B.F.G.Johnson), Wiley, Chichester, 1980, p.195.
3. D.M.P.Mingos, Adv.Organometal.Chem., 1977, **15**, 1.
4. P.Chini, J.Organometal.Chem., 1980, **200**, 37.
5. E.L.Muetterties, J.Organometal.Chem., 1980, **200**, 177.
6. B.F.G.Johnson and R.E.Benfield, Topics in Stereochem., 1981, **12**, 254; in "Transition Metal Clusters" (Edited by B.F.G.Johnson), Wiley, Chichester, 1980, p.472.
7. P.R.Raithby, in "Transition Metal Clusters" (Edited by B.F.G.Johnson), Wiley, Chichester, 1980, p.7.
8. C.D.Garner, in "Transition Metal Clusters" (Edited by B.F.G.Johnson), Wiley, Chichester, 1980, p.267.
9. R.G.Wooley, in "Transition Metal Clusters" (Edited by B.F.G.Johnson), Wiley, Chichester, 1980, p.607.
10. D.A.Lemenovskii, Izv.Sibir.Otd.Akad.Nauk SSSR, Ser.Khim., 1982, **4**, 5.
11. V.I.Minkin and R.M.Minyaev, Uspekhi Khim., 1982, **51**, 586 [Russ.Chem.Rev., 1982(4)].
12. F.A.Cotton and T.E.Haas, Inorg.Chem., 1964, **3**, 10.
13. E.R.Corey, L.F.Dahl, and W.Beck, J.Amer.Chem. Soc., 1963, **85**, 1202.
14. G.G.Aleksandrov, G.P.Zol'nikova, I.I.Kritskaya, and Yu.T.Struchkov, Koord.Khim., 1980, **6**, 626.
15. F.A.Cotton and J.M.Troup, J.Amer.Chem.Soc., 1974, **96**, 4155.
16. A.A.F.Maria, C.G.Carrondo, and A.C.Skapski, Chem.Comm., 1976, 410.
17. M.R.Churchill and R.Bau, Inorg.Chem., 1968, **7**, 2606.
18. C.H.Wei, Inorg.Chem., 1969, **8**, 2384.
19. A.A.Pasynskii, I.L.Eremenko, B.Orazsakhatov, V.T.Kalinnikov, G.G.Aleksandrov, and Yu.T.Struchkov, J.Organometal.Chem., 1981, **214**, 367.
20. V.G.Albano, M.Sansoni, P.Chini, and S.Martinengo, J.Chem.Soc., Dalton Trans., 1973, 651.
21. L.D.Lower and L.F.Dahl, J.Amer.Chem.Soc., 1916, **98**, 5046.
22. J.W.Lauher, J.Amer.Chem.Soc., 1978, **100**, 5305; J.Amer.Chem.Soc., 1979, **101**, 2604.
23. J.W.Lauher, J.Catalysis, 1980, **66**, 237; J.Organometal.Chem., 1981, **213**, 25.
24. G.Ciani and A.Sironi, J.Organometal.Chem., 1980, **197**, 233.
25. R.Hoffman, B.E.R.Schilling, R.Bau, H.D.Kaesz, and D.M.P.Mingos, J.Amer.Chem.Soc., 1978, **100**, 6088.
26. K.Wade, Chem.Comm., 1971, 792.
27. W.N.Lipscomb, "Boron Hydrides", Benjamin Press, New York, 1963.
28. M.E.Dyatkina, Zhur.Vses.Khim.Obshch.im. Mendeleeva, 1972, **17**, 285.
29. P.F.Jackson, B.F.G.Johnson, J.Lewis, M.McPartlin, and W.J.H.Nelson, Chem.Comm., 1980, 224.
30. P.L.Bellon, M.Manassero, and M.Sansoni, J.Chem. Soc.Dalton Trans., 1973, 2423.
31. D.M.P.Mingos, J.Chem.Soc.Dalton Trans., 1976, 1163; Pure and Appl.Chem., 1980, **52**, 705.
32. C.E.Briant, B.R.C.Theobald, J.W.White, L.K.Bell, D.M.P.Mingos, and A.J.Welch, Chem.Comm., 1981, 201.
33. D.G.Evans and D.M.P.Mingos, J.Organometal.Chem., 1982, **232**, 171.
34. D.G.Evans and D.M.P.Mingos, Organometallics, 1983, **2**, 435.
35. D.G.Evans and D.M.P.Mingos, J.Organometal. Chem., 1982, **240**, 321.
36. M.Elian, M.M.L.Chen, D.M.P.Mingos, and R.Hoffman, Inorg.Chem., 1976, **15**, 1148.
37. K.Burgess, B.F.G.Johnson, D.A.Kaner, J.Lewis, P.R.Raithby, S.N.Azman, and B.Syed-Mustaffa, Chem.Comm., 1983, 455.
38. L.W.Bateman, M.Green, J.A.K.Howard, K.A.Mead, R.W.Mills, I.D.Salter, F.G.A.Stone, and P.Woodward, Chem.Comm., 1982, 773.
39. N.Trinaistich, in "Semiempirical Methods for the Calculations of Electronic Structures" (Translated into Russian), Izd.Mir, Moscow, 1980, p.13.
40. R.B.King and D.H.Rouvray, J.Amer.Chem.Soc., 1977, **99**, 7834; Theor.Chim.Acta, 1978, **48**, 207.
41. A.J.Stone, Inorg.Chem., 1981, **20**, 563.
42. A.Messiah, "Quantum Mechanics" (Translated into Russian), Izd.Mir, Moscow, 1979, **2**, 24.
43. L.Pauling, "The Nature of the Chemical Bond" (Translated into Russian), Goskhimizdat, Moscow–Leningrad, 1947, p.392.
44. R.Mason, Pure and Appl.Chem., 1973, **33**, 513.
45. R.D.Wilson and R.Bau, J.Amer.Chem.Soc., 1976, **98**, 4687.
46. G.Hüttner and H.Lorenz, Chem.Ber., 1974, **107**, 996.
47. H.D.Kaesz, B.Fontal, R.Bau, S.W.Kirtley, and M.R.Churchill, J.Amer.Chem.Soc., 1969, **91**, 1021.
48. G.Hüttner and H.Lorenz, Chem.Ber., 1974, **108**, 973.
49. J.A.Bertrand, F.A.Cotton, and W.A.Dollase, Inorg. Chem., 1963, **2**, 1166.
50. C.D.Garner, Coord.Chem.Reviews, 1982, **85**, 153.
51. M.B.Hursthouse and K.M.Abdul Malik, J.Chem. Soc., Dalton Trans., 1978, 1334.
52. M.J.Bennett, W.A.G.Graham, J.K.Hoyano, and W.L.Hutcheon, J.Amer.Chem.Soc., 1972, **94**, 6232.
53. S.Otsuka, Y.Tatsuno, M.Miki, T.Aoki, M.Matsumoto, H.Yoshioka, and K.Nakatsku, Chem.Comm., 1973, 445.
54. P.W.Frost, J.A.K.Howard, J.L.Spencer, D.G.Turner, and D.Gregson, Chem.Comm., 1981, 1104.
55. M.Green, J.A.K.Howard, J.L.Spencer, and F.G.A.Stone, Chem.Comm., 1975, 3.
56. A.Albinati, G.Carturan, and A.Musco, Inorg. Chim.Acta, 1976, **16**, L3.
57. E.G.Mednikov, N.K.Eremenko, and S.P.Gubin, Koord.Khim., 1984, **10**, 711.
58. M.N.Vargaftik, T.A.Stromnova, T.S.Khodasheva, M.A.Porai-Koshits, and I.I.Moiseev, Koord.Khim., 1981, **7**, 132.
59. R.G.Vranka, L.F.Dahl, P.Chini, and J.Chatt, J. Amer.Chem.Soc., 1969, **91**, 1574.
60. E.G.Mednikov, N.K.Eremenko, S.P.Gubin, Yu.L.Slovokhotov, and Yu.T.Struchkov, J. Organometal.Chem., 1982, **239**, 401.
61. J.-P.Barbier, R.Bender, P.Braunstein, J.Fischer, and L.Ricard, J.Chem.Res., 1978, **230**, 2913.
62. A.Albinata, A.Moor, P.S.Pregosin, and L.M.Venanzi, J.Amer.Chem.Soc., 1982, **104**, 7672.
63. Ya.Yamamoto, H.Yamazaki, and T.Sakurai, J.Amer. Chem.Soc., 1982, **104**, 2329.
64. E.G.Mednikov, V.V.Bashilov, V.I.Sokolov, Yu.L.Slovokhotov, and Yu.T.Struchkov, Polyhedron, 1983, **2**, 141.

65. J.A.J.Jarvis, B.T.Kilbourn, R.Pearce, and M.F.Lappert, Chem.Comm., 1973, 475.
66. A.N.Nesmeyanov, Yu.T.Struchkov, N.N.Sedova, V.G.Andrianov, Yu.V.Volgin, and V.A.Sazonova, J.Organometal.Chem., 1977, 137, 217.
67. A.N.Nesmeyanov, N.N.Sedova, Yu.T.Struchkov, V.G.Andrianov, E.N.Stakheeva, and V.A.Sazonova, J.Organometal.Chem., 1978, 153, 115.
68. T.Greiser and E.Weiss, Chem.Ber., 1976, 109, 3142.
69. D.Coucouvanis, C.N.Murphy, and S.K.Kanodia, Inorg.Chem., 1980, 19, 2993.
70. C.L.Raston and A.H.White, J.Chem.Soc., Dalton Trans., 1976, 2153.
71. J.J.Guy, P.G.Jones, M.J.Mays, and G.M.Sheldrick, J.Chem.Soc., Dalton Trans., 1977, 8.
72. F.Demartin, M.Manassero, L.Naldini, R.Ruggero, and M.Sansoni, Chem.Comm., 1981, 222.
73. J.W.A.van der Velden, J.J.Bour, V.A.Vollenbroek, P.T.Beurskens, and J.M.M.Smits, Chem.Comm., 1979, 1162.
74. A.N.Nesmeyanov, E.G.Perevalova, Yu.T.Struchkov, M.Yu.Antipin, and V.P.Djadchenko, J.Organometal. Chem., 1980, 201, 343.
75. P.G.Jones, G.M.Sheldrick, and E.Hadicke, Acta Cryst., 1980, B36, 2777.
76. I.Shapiro, C.D.Good, and R.E.Williams, J.Amer. Chem.Soc., 1962, 84, 3837.
77. P.A.Edwards and J.D.Corbett, Inorg.Chem., 1977, 16, 903.
78. C.R.Eady, B.F.G.Johnson, J.Lewis, B.E.Reichert, and G.M.Sheldrick, Chem.Comm., 1976, 271.
79. A.Fumagalli, T.F.Koetzle, and F.Takusagawa, J. Organometal.Chem., 1981, 213, 365.
80. Y.C.Lin, C.B.Knobler, and H.D.Kaesz, J.Organometal.Chem., 1981, 213, C41.
81. D.Braga, B.F.G.Johnson, J.Lewis, J.M.Mace, M.McPartlin, J.Puga, W.J.H.Nelson, P.R.Raithby, and K.H.Whitmire, Chem.Comm., 1982, 1081.
82. C.A.Chilardi, S.Midollini, and L.Sacconi, Inorg. Chim.Acta, 1978, 31, L431.
83. M.I.Bruce and B.K.Nicholson, Chem.Comm., 1982, 1141.
84. A.A.Pasynskii, I.L.Eremenko, B.Orazsakhatov, Yu.V.Rakitin, V.M.Novotortsev, O.G.Ellert, V.T.Kalinnikov, G.G.Aleksandrov, and Yu.T.Struchkov, J.Organometal.Chem., 1981, 214, 351.
85. F.Bottomley and P.S.White, Chem.Comm., 1981, 28.
86. P.D.Frisch and L.F.Dahl, J.Amer.Chem.Soc., 1972, 94, 5082.
87. G.Longoni, P.Chini, L.D.Lower, and L.F.Dahl, J.Amer.Chem.Soc., 1975, 97, 5034.
88. H.Vahrenkamp, V.A.Uchtman, and L.F.Dahl, J. Amer.Chem.Soc., 1968, 90, 3272.
89. D.W.Hart, R.G.Teller, C.-Y.Wei, R.Bau, G.Longoni, S.Campanella, P.Chini, and T.F.Koetzl, Angew. Chem.Int.Ed., 1979, 18, 80.
90. R.Mason and W.R.Robinson, Chem.Comm., 1968, 468.
91. J.C.Huffman, J.G.Stone, W.C.Krusekl, and K.G.Caulton, J.Amer.Chem.Soc., 1977, 99, 5829.
92. P.F.Jackson, B.F.G.Johnson, J.Lewis, P.R.Raithby, G.J.Will, M.McPartlin, and W.J.H.Nelson, Chem. Comm., 1980, 1190.
93. B.F.G.Johnson, D.A.Kaner, J.Lewis, P.R.Raithby, and M.J.Rosales, J.Organometal.Chem.,1982, 231, C59.
94. V.E.Lopatin, N.M.Mikova, and S.P.Gubin, Izv. Akad.Nauk SSSR, Ser.Khim., 1981, 1925.
95. M.Tachikawa, J.Stein, E.L.Muetterties, R.G.Teller, M.A.Beno, E.Gebert, and J.M.Williams, J.Amer. Chem.Soc., 1980, 102, 6648.
96. B.F.G.Johnson, J.Lewis, J.N.Nichols, I.A.Oxton, P.R.Raithby, and M.J.Rosales, Chem.Comm., 1982, 289.
97. M.S.Paquette and L.F.Dahl, J.Amer.Chem.Soc., 1980, 102, 6621.
98. F.Cecconi, C.A.Chilardi, and S.Midollini, Chem. Comm., 1981, 640.
99. J.D.Corbett, R.L.Daake, K.R.Poeppelmeier, and D.H.Guthrie, J.Amer.Chem.Soc., 1978, 100, 652.
100. F.W.Koknat and R.E.McCarley, Inorg.Chem., 1972, 11, 812.
101. A.Simon, H.G.Schnering, H.Wohrle, and H.Schafer, Z.anorg.Chem., 1965, 339, 155.
102. S.S.Basson and J.G.Leipoldt, Transition Metal Chemistry, 1982, 7, 207.
103. R.Siepmann, H.G.Schnering, and H.Schafer, Angew.Chem., 1967, 79, 650.
104. H.Imoto and J.D.Corbett, Inorg.Chem., 1980, 19, 1241.
105. P.C.Healy, D.L.Kepert, D.Taylor, and A.H.White, J.Chem.Soc., Dalton Trans., 1973, 648.
106. M.R.Churchill and S.A.Bezman, Inorg.Chem., 1974, 13, 1418.
107. S.A.Bezman, M.R.Churchill, J.A.Osborn, and J.Wormald, J.Amer.Chem.Soc., 1971, 93, 2063.
108. J.M.Guss, R.Mason, K.M.Thomas, G.van Koten, and J.G.Noltes, J.Organometal.Chem., 1972, 40, C79.
109. R.W.M.ten Hoedt, J.G.Noltes, G.van Koten, and A.L.Spek, J.Chem.Soc., Dalton Trans., 1978, 1800.
110. H.Dietrich, W.Storck, and G.Manecke, Chem.Comm., 1982, 1036.
111. J.W.A.van der Velden, J.J.Bour, B.F.Otterloo, W.P.Bosman, and J.H.Noordik, Chem.Comm., 1981, 583.
112. V.G.Albano, P.L.Bellon, and G.F.Ciani, Chem.Comm., 1969, 1024.
113. P.F.Jackson, B.F.G.Johnson, J.Lewis, and P.R.Raithby, Chem.Comm., 1980, 60.
114. G.Ciani, G.D'Alfonso, M.Freni, P.Romiti, and A.Sironi, Chem.Comm., 1982, 705.
115. D.Braga, K.Henrick, B.F.G.Johnson, J.Lewis, M.McPartlin, and W.J.H.Nelson, Chem.Comm., 1982, 1083.
116. R.Goddard, P.W.Jolly, C.Krüger, K.-P.Schick, and G.Wilke, Organometallics, 1982, 1, 1709.
117. R.A.Jones, F.M.Real, G.Wilkinson, A.M.R.Galas, and M.B.Hursthouse, J.Chem.Soc., Dalton Trans., 1981, 126.
118. G.Longoni, M.Manassero, and M.Sansoni, J.Amer. Chem.Soc., 1980, 102, 7973.
119. Yu.L.Slovokhotov and Yu.T.Struchkov, J.Organometal.Chem., 1983, 258, 47.
120. D.M.P.Mingos, Chem.Comm., 1983, 706.
121. S.Martinengo, A.Fumagalli, R.Bonfichi, G.Ciani, and A.Sironi, Chem.Comm., 1982, 825.
122. C.M.Hayward, J.R.Shapley, M.R.Churchill, C.Bueno, and A.L.Rheingold, J.Amer.Chem.Soc., 1982, 104, 7347.
123. R.C.Eady, J.M.Fernandez, B.F.G.Johnson, J.Lewis, P.R.Raithby, and G.M.Sheldrick, Chem.Comm., 1978, 421.
124. A.Fumagalli, S.Martinengo, G.Ciani, and A.Sironi, Chem.Comm., 1983, 453.
125. J.L.Vidal, W.E.Walker, R.L.Pruett, and R.C.Schoening, Inorg.Chem., 1979, 18, 129.
126. J.L.Vidal, Inorg.Chem., 20, 243.

127. G.Ciani, G.Garlaschelli, A.Sironi, and S.Martinengo, Chem.Comm., 1981, 563.
128. R.S.Burns and J.D.Corbett, J.Amer.Chem.Soc., 1982, 104, 2804.
129. V.G.Albano, P.Chini, G.Ciani, S.Martinengo, and M.Sansoni, J.Chem.Soc., Dalton Trans., 1978, p.463.
130. V.G.Albano, D.Braga, G.Ciani, and S.Martinengo, J.Organometal.Chem., 1981, 213, 293.
131. V.G.Albano, P.Chini, S.Martinengo, N.Sansoni, and D.Strumolo, J.Chem.Soc., Dalton Trans., 1978, 459.
132. S.Martinengo, G.Ciani, and A.Sironi, J.Amer.Chem. Soc., 1982, 104, 328.
133. J.D.Corbett, Progr.Inorg.Chem., 1980, 21, 129.
134. R.N.Grimes, "Carboranes" (Translated into Russian), Izd.Mir, Moscow, 1974.
135. J.L.Vidal and J.M.Troup, J.Organometal.Chem., 1981, 213, 351.
136. J.W.A.van der Velden, J.J.Bour, W.P.Bosman, and J.H.Noordik, Chem.Comm., 1981, 1218.
137. P.L.Bellon, F.Cariati, M.Manassero, L.Naldini, and M.Sansoni, Chem.Comm., 1971, 1423.
138. M.V.Cooper, G.R.Dennis, K.Henrick, and M.McPartlin, Inorg.Chim.Acta, 1980, 45, 151.
139. P.M.van Attekum, J.W.A.van der Velden, and J.M.Trooster, Inorg.Chem., 1980, 19, 701.
140. K.P.Hall, B.R.C.Theobald, D.I.Gilmour, D.M.P.Mingos, and A.J.Welch, Chem.Comm., 1982, 528.
141. V.G.Albano, A.Ceriotti, P.Chini, G.Ciani, S.Martinengo, and M.Anker, Chem.Comm., 1975, 859.
142. G.Ciani, A.Sironi, and S.Martinengo, J.Organometal. Chem., 1980, 192, C42.
143. S.Martinengo, G.Ciani, A.Sironi, and P.Chini, J. Amer.Chem.Soc., 1978, 100, 7096.
144. J.L.Vidal, L.A.Kapicak, and J.M.Troup, J.Organometal.Chem., 1981, 215, C11.
145. G.Ciani, A.Magni, A.Sironi, and S.Martinengo, Chem.Comm., 1981, 1280.
146. J.L.Vidal, R.C.Schoening, and J.M.Troup, Inorg. Chem., 1981, 20, 227.
147. D.M.Washecheck, E.J.Wucherer, L.F.Dahl, A.Ceriotti, G.Longoni, M.Manassero, M.Sansoni, and P.Chini, J.Amer.Chem.Soc., 1979, 101, 6110.
148. D.M.P.Mingos and D.G.Evans, J.Organometal. Chem., 1983, 251, C13.
149. B.K.Teo and K.Keating, J.Amer.Chem.Soc., 1984, 106, 2224.
150. B.K.Teo, Chem.Comm., 1983, 1362.

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