

A SIMPLE TOPOLOGICAL MODEL OF A SUPERAROMATIC CLUSTER AND SOME DIFFICULTIES OF THE ELECTRON COUNTING SCHEME

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Summary

A simple model of the conductive surface, which is topologically equivalent to the superaromatic polyhedral system, defines the class of "Wade's" clusters obeying the $2n + 2$ rule and extends the electron counting procedure to superaromatic *conjuncto*-clusters.

Introduction

From the time when the $2n + 2$ rule was formulated by Wade and the counting scheme for cluster skeletal electrons worked out [1], the limits of the rule and its physical implication have continued to be discussed. During the last decade the magic numbers of skeletal electrons in polyhedral molecules have been discussed and their validity substantiated within the scope of different approaches: qualitative molecular orbital considerations [1,2], extended Hückel MO's [3,4], graph theory [5], the conductive sphere model [6] and several others. At the same time, attempts have been made to establish similar magic numbers for the clusters of the platinum metals and gold [7], which usually do not obey the $2n + 2$ rule.

In spite of a substantial number of papers, the theory of cluster bonding remains, however, unaccomplished and the Wade's rule still appears to be "semiempirical". The most prominent results in this field have been achieved using physical models, which reflect fundamental properties of the clusters [5,6]. Considering this approach to be very fruitful we now attempt to give a definition of a superaromatic cluster on the basis of a simple topological model.

Discussion

All cluster molecules whose structures have been studied may now be roughly subdivided into "Wade's" and "non-Wade's" systems in accordance with the $2n + 2$ rule, which in these cases is, respectively, valid or non-valid (Table 1). "Non-Wade's"

TABLE 1
TYPES OF CLUSTERS AND REPRESENTATIVE SPECIES

I "Wade's" clusters	II "Non-Wade's" clusters
1 Boron hydrides, carboranes, metallocarboranes ($B_{10}H_{14}$, $C_2B_{10}H_{12}$, $CpCoC_2B_9H_{11}$, etc.)	1 Clusters with localized bonds (tetrahedron, trigonal prism, cube)
2 Organometallic complexes with η -olefin ligands and $18e$ valence shell of the metal atom ($CpMn(CO)_3$, $C_6H_6Cr(CO)_3$, Cp_2Fe , etc.)	2 Trigonal bipyramid ($Cp_5V_5O_6$, etc. [11])
3 Octahedral carbonyl clusters of transition metals and their derivatives ($Rh_6(CO)_{16}$, $Fe_5C(CO)_{15}$)	3 Large metaloclusters ($Rh_{13}(CO)_{25}H_{5-n}^{n-}$, $Rh_{22}(CO)_{37}^{4-}$, etc. [12])
4 Capped square antiprism ($Rh_{10}S(CO)_{22}^{2-}$ [8], $Rh_9P(CO)_{21}^{2-}$ [9], etc.)	4 "Inorganic" halogenide clusters ($Mo_6Cl_8^{4+}$, $Nb_6Cl_{12}^{2+}$)
5 Polynuclear non-transition metal cluster ions (Sn_8Ti^{3-} , Sn_9Ti^{-} [10])	5 Clusters of platinum and post-transition metals

clusters (the second column of Table 1) include very different polyhedra wherein this rule is not fulfilled at all (noble metal clusters, large metaloclusters) or frequently violated (trigonal bipyramid, nickel clusters). Several types of such clusters may be described satisfactorily by alternative methods: for example, clusters of the type II.1 are considered to have only localised two-centre two-electron bonds, so the octet rule and/or the effective atomic number rule (EAN or $18e$) are satisfied for their atoms, depending on the types of these atoms; the large metaloclusters (II.3) are well described by zone theory [13], etc. On the other hand, in the relatively limited group of polyhedra (octahedron, capped square antiprism, icosahedron) built up of some particular atoms (usually boron, carbon and middle transition metals) the $2n + 2$ rule is fulfilled surprisingly well (the first column of Table 1). The question naturally arises — is Wade's rule of general application and which clusters can in principle obey it?

At present it is customary to regard the cluster polyhedral unit as a three-dimensional superaromatic system with a sufficient delocalisation of bonding electrons over the polyhedron. This point of view, although correct for a definite group of polynuclear complexes, seems yet to be, strictly speaking, non-valid for cluster compounds as a whole. For example, contemporary experimental data evidently leads to the conclusion that not every cluster molecule exhibits superaromaticity as well as only several cyclic molecules possess delocalized π -aromatic Hückel systems ($4n + 2$ π -electrons). The simple topological model of π -aromatic systems represents a conductive ring. Similarly, all available structural data allows us to draw the following conclusion:

Only "Wade's" clusters, obeying the $2n + 2$ rule, are superaromatic systems. These and only these clusters are topologically equivalent to a continuous closed conductive surface with a small cavity inside it.

This simple topological model of the superaromatic cluster results directly from the paper by King and Rouvray [5], who have used the very important (although strictly unproven) postulate of the splitting of cluster MO's into exopolyhedral, tangential and internal; and from the Stone's spherical shell model [6], though, however, the spherical symmetry of the system seems not to be sufficient and the

determining characteristic is the connectivity of cluster polyhedron. The superaromatic "Wade's" clusters (Table 1) include simple deltahedra with the number of vertices $n \leq 13$, which may have several open faces (*nido* and *arachno* frameworks) and/or an interstitial atom of a light element. The small size of the cavity must satisfy the condition of a mutual overlap of internal MO's [5], while the continuity of the conductive surface reflects a delocalisation of tangential bonding. Appearance of an open face in *nido* and *arachno* polyhedra corresponds to the puncturing of the continuous conductive surface, which, according to King and Rouvray, leads to increasing bond localisation in the cluster.

On the basis of the simple topological model, the selection of "Wade's" clusters among the others can be substantiated. Actually, all "non-Wade's" clusters in the second column of Table 1 do not correspond to the model of the closed conductive surface, because of bond localisation, a large number of open faces, the presence of metal crystal lattice fragments inside the polyhedron, and so on. The specific position of a trigonal bipyramid (II.2) can also be reasonably explained, since this *conjuncto*-polyhedron represents a system of two face-condensed tetrahedra (i.e. "localized" polyhedra, II.1) cut through the middle by a common trigonal "delta" face and so topologically non-equivalent to a "delocalized" closed surface with a single cavity inside it. Really the relevant magic number of skeletal electrons (12) is very often violated in trigonal bipyramidal clusters, whereas the great majority of octahedral derivatives appear to be "Wade's" clusters. Moreover, the model allows rationalization of the violation of the $2n + 2$ rule in clusters with a large internal cavity (for example, in 14-vertex tetracarbon metallocarboranes [14]). A poor overlap of internal MO's requires the introduction of a bonding centre into the polyhedron, and in fact all recently synthesised capped square-antiprismatic rhodium clusters contain an interstitial P, S, or As atom inside a large polyhedral cavity [8,9].

By this approach it is not so easy to explain why octahedral halogenide clusters of the early transition metals (Mo, Nb) are of the "non-Wade's" type. One possible explanation was suggested by Wade, who proposed localisation of metal-metal bonds in these clusters [13]; an alternative point of view takes into account the limiting donating abilities of the halogen atoms in the dense coordination sphere enveloping the metal octahedron. At any rate it is interesting to note, that "Wade's" clusters are usually built up of the metals which acquire the $18e$ configuration in their mononuclear derivatives. For post-transition metals, along with an increase in stability of $16e$ or $14e$ valence shells and a drop of the coordination ability in mononuclear complexes, both the EAN and $2n + 2$ rules become invalid. The inclusion of a post-transition metal atom in the framework of a metallocarborane [15] or η -cyclopentadienyl complex [16] leads to the opening of the cluster polyhedron, i.e. to a puncturing of the conductive deltahedral surface of the tangential bonding without the required addition of skeletal electrons. Thus, increase in the number of post-transition metal atoms in the cluster framework must lead to increased puncturing of the tangential bonding surface, therefore the deltahedral surface of "non-Wade's" *closo*-clusters such as $[\text{Au}_6(\text{PR}_3)_6]^{2+}$ [17] or $[\text{Cu}_6\text{H}_6(\text{PR}_3)_6]^{2+}$ [18] is evidently not continuously conductive.

Apart from the selection of superaromatic "Wade's" systems, the topological model enables the extension of the $2n + 2$ rule to *conjuncto*-clusters. Two "Wade's" n -vertex deltahedra may, in principle, have a common vertex, a common edge, or a common face (Fig. 1). In the first case, the topological model of the cluster

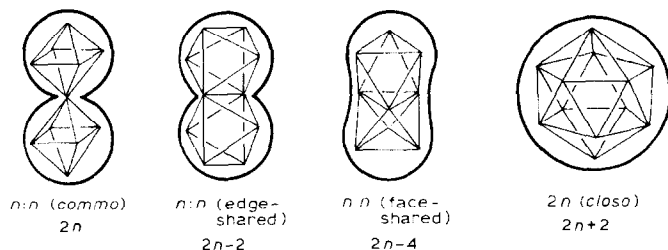


Fig. 1. Topological models of *commo*-, edge-shared and face-shared bis- n -vertex polyhedra, and *closo*- $2n$ -vertex clusters, with the number of skeletal electrons therein.

represents two closed surfaces with one common punctured point; in the second case, similar surfaces with a common “punctured” segment; and in the third one, the single enveloping closed surface with a constriction. All of these three-dimensional surfaces can be transformed one into another, as well as into any other closed surface with a single cavity, by continuous deformations in three-dimensional space, and therefore these surfaces are homeomorphous. Assuming that the polyhedral surface is still continuously conductive we can extend the $2n + 2$ rule to condensed clusters with the following modification:

The number of skeletal electrons in a conjuncto-cluster is counted by the usual scheme, but the vertices common to adjacent polyhedra are excluded from the total number of cluster vertices.

The suggested modification to the counting scheme resembles the generalisation of the Hückel's rule for condensed aromatic rings [19] and allows true magic numbers to be obtained for poly-polyhedral clusters. In accordance with this modified scheme, the anionic $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ *commo*-metallo-carborane [20] is equivalent to a *closo*-22-vertex polyhedron and correspondingly has 46 skeletal electrons, and the ferrocene molecule (with 26 skeletal electrons) is equivalent to an *arachno*-10-vertex polyhedron, etc.

The electron counting procedure for *commo*-metallo-carboranes has been used up to now without the topological model, although the latter provides more generality. Nevertheless, a search for magic numbers in recently-synthesised *conjuncto*-clusters with a common edge or a common face encountered some difficulties, whilst in our approach these numbers can be obtained simply and unequivocally. Thus, two octahedra with a common face are equivalent to a *closo*-6-vertex deltahedron and two octahedra with a common edge to a *closo*-8-vertex deltahedron. The first *conjuncto*-cluster must therefore have 14 skeletal electrons and the second one must have 18e, which is just the case in the structures of $[\text{Rh}_9(\text{CO})_{19}]^{3-}$ [21] and $[\text{Ru}_{10}(\text{C})_2(\text{CO})_{24}]^{2-}$ [22], respectively. Moreover, on the basis of the suggested scheme it becomes possible to rationalize the structures of the challenging *conjuncto*-platinaborane systems [23], bearing in mind a necessary correction for polyhedra distortion due to the presence of a Pt atom (*vide supra*). Within our approach the structures of three isomeric 19-vertex $\text{L}_2\text{PtB}_{18}\text{H}_{20}$ derivatives may be regarded as equivalent to a *hypho*-16-vertex polyhedron (*nido*: *arachno* bisicosahedral clusters with one common face) and therefore must have 40 skeletal electrons, which they actually do; the face-condensed thermolysis product $\text{L}_2\text{Pt}(\eta^4\text{-anti-B}_{18}\text{H}_{18})$, being equivalent to an *arachno*-16-vertex polyhedron, must have 38 skeletal electrons, which is the case, as it is with the diplatinum-cluster $\text{L}_4\text{Pt}_2(\eta^4: \eta^4 + \eta^2\text{-anti-B}_{18}\text{H}_{16})$,

which is equivalent to a *nido*-17-vertex polyhedron. So the Wade's rule may be extended to sufficiently complicated *conjuncto*-polyhedra.

Conclusion

It should be stressed that the qualitative physical model, which reflects the topology of superaromatic cluster bonding, already allows: (1) a definition of the class of "superaromatic" polyhedral derivatives, where the $2n + 2$ rule is valid, and (2) the extension of this rule to condensed "Wade's" clusters. The Wade's rule itself appears to be closely related not only to the Hückel's rule for "classical" aromatic systems, as has been pointed out earlier [5], but also to the EAN rule for mononuclear metal complexes. The proper search for the magic numbers, if any, in post-transition metal clusters must evidently include an analysis of the electronic structures of their atoms, in particular the reasons for the stability of $16e$ and $14e$ configurations, where the valence shell of atom is not fully occupied.

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Note added in proof: After this paper was submitted to publication, D.M.P. Mingos has proposed the other rules for magic numbers in any shared polyhedral clusters based on another scheme (D.M.P. Mingos, J. Chem. Soc., Chem. Commun., (1983) 706). For the condensed superaromatic deltahedra both approaches lead to the same predictions providing the further evidence for the topological model.