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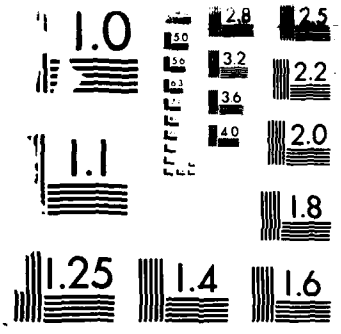
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by

R.B. King

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University of Georgia
Department of Chemistry
Athens, GA 30602

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GRAPH THEORY DERIVED METHODS FOR THE STUDY OF METAL CLUSTER BONDING TOPOLOGY: APPLICATIONS TO POST-TRANSITION METAL CLUSTERS

R.B. King

Department of Chemistry
University of Georgia
Athens, Georgia 30602, U.S.A.

ABSTRACT

Graph-theory derived methods have been used to study the chemical bonding topology of clusters of post-transition metals such as Sn, Pb, Sb, and Bi thereby suggesting that similar structure and bonding ideas apply to both condensed phase and gas phase clusters of these metals.

INTRODUCTION

Several years ago we developed a graph-theoretical approach for the study of the bonding topology in polyhedral boranes, carboranes, and metal clusters.[1,2] Subsequent work has shown this approach to be very effective in relating electron count to cluster shape for diverse metal clusters using a minimum of computation. Examples of metal clusters treated effectively by this approach include condensed phase post-transition metal clusters[3] as well as osmium carbonyl clusters,[4] gold clusters,[5,6] platinum carbonyl clusters,[5,7] and rhodium carbonyl clusters having fused polyhedra.[8,9]

Recent experimental work by Duncan and collaborators[10,11,12] indicates that laser vaporization of post-transition metals such as tin, lead, antimony, bismuth, and their alloys in a supersonic molecular beam apparatus[13] leads to gas phase metal clusters having unusual local maxima in their cluster size distributions. This paper summarizes an initial attempt to relate these "magic numbers" to the graph-theory derived and related metal cluster bonding models thereby demonstrating apparent connections between the structure and bonding of metal clusters in the condensed and gas phases.

BACKGROUND

The topology of chemical bonding can be represented by a graph in which the vertices correspond to atoms or orbitals participating in the bonding and the edges correspond to bonding relationships. The eigenvalues x of the adjacency matrix of such a graph are related to the Hückel theory molecular orbital energies E and the Hückel parameters α and β by the following equation[1,2,3,9,14,15]:

$$E = \frac{\alpha + x\beta}{1 + xS} \qquad (1)$$

Positive and negative eigenvalues x thus correspond to bonding and antibonding orbitals, respectively.

The two extreme types of chemical bonding in metal clusters may be called edge-localized and globally delocalized.[1,2] An edge-localized polyhedron has two-electron two-center bonds along each edge of the polyhedron and is favored when the numbers of internal orbitals of the vertex atoms match the vertex degrees. (The number of edges meeting at a vertex is its degree.) Since vertex atoms in metal clusters normally use three internal orbitals for cluster bonding, cluster polyhedra exhibiting pure edge-localized bonding normally have only degree three vertices (e.g., the tetrahedron, cube, or various prisms). A globally delocalized polyhedron has a multicenter core bond in the center of the polyhedron and is favored when the numbers of internal orbitals do not match the vertex degrees.

One of the major triumphs of the graph-theory derived approach to the bonding topology in globally delocalized systems is the demonstration of the close analogy between the bonding in two-dimensional planar polygonal aromatic systems such as benzene and that in three-dimensional boranes and carboranes based on deltahedra without tetrahedral chambers.[1,2,9] In both cases the three internal orbitals from each vertex are partitioned into two twin internal orbitals and a single unique internal orbital. In the two-dimensional planar polygonal systems the twin internal orbitals overlap pairwise to form the so-called σ-bonding network around the circumference of the polygon and the unique internal orbitals overlap cyclically (C_n graph) to form the so-called π-bonding network. In the three-dimensional deltahedral systems the twin internal orbitals overlap pairwise in the surface of the polyhedron and the unique internal orbitals form a multicenter core bond (K_n graph) at the center of the polyhedron. Both of these types of bonding are found in post-transition metal clusters.

The globally delocalized deltahedra with n vertices have 2n + 2 skeletal electrons with 2n of these electrons arising from the surface bonding and the remaining 2 electrons occupying the single molecular orbital arising from the multicenter core bond.[1,2] Electron-rich polyhedra having more than 2n + 2 apparent skeletal electrons have one or more non-triangular faces whereas electron-poor deltahedra having less than 2n + 2 apparent skeletal electrons have one or more tetrahedral chambers. Several examples of so-called nido electron-rich polyhedra having precisely 2n + 4 skeletal electrons are encountered in post-transition metal clusters. All but one of the faces of nido polyhedra are triangles. If a deltahedron having 2n + 2 skeletal electrons is regarded as topologically homeomorphic to a sphere, then a nido polyhedron having 2n + 4 skeletal electrons is topologically homeomorphic to a sphere with a hole in it corresponding to the single non-triangular face.

The general approach for considering metal cluster bonding models involves calculating the number of available skeletal electrons for comparison with the numbers of skeletal electrons required to fill the bonding molecular orbitals for various cluster shapes and bonding topologies. If vertex atoms furnishing the normal 3 internal orbitals are considered, then Sn and Pb vertices like BH, $Fe(CO)_3$, and C_5H_5Co vertices are donors of 2 skeletal electrons and Sb and Bi vertices like CH, $Co(CO)_3$, and C_5H_5Ni vertices are donors of 3 skeletal electrons.[3] Such relationships provide isoelectronic and isolobal analogies of bare post-transition metal clusters to planar aromatic hydrocarbons, polyhedral boranes, and/or transition metal clusters having external carbonyl, hydrocarbon, and/or phosphine ligands.

APPLICATIONS TO POST-TRANSITION METAL CLUSTERS

Condensed Phases

The condensed-phase bare post-transition metal cluster ions reviewed by Corbett[16] and discussed partially in an earlier paper[3] have been found by X-ray crystallography to have the following structures for which the indicated chemical bonding topologies may be proposed:

Square. Bi_4^{2-}, Se_4^{2+} and Te_4^{2+} isoelectronic and isolobal with the cyclobutadiene dianion with 14 skeletal electrons, 8 for the 4 σ bonds and 6 for the π-bonding.

Tetrahedron. $Pb_2Sb_2^{2-}$ with 12 skeletal electrons for localized bonds along the 6 edges of the tetrahedron analogous to organic tetrahedrane derivatives, R_4C_4.

Trigonal bipyramid. Sn_5^{2-}, Pb_5^{2-}, and Bi_5^{3+} with 12 skeletal electrons analogous to the $C_2B_3H_5$ carborane.

Capped square antiprism. Ge_9^{4-}, Sn_9^{4-}, and Pb_9^{4-} with the $2n + 4 = 22$ skeletal electrons required for an $n = 9$ vertex C_{4v} nido polyhedron having 12 triangular faces and one square face.

Tricapped trigonal prism. Ge_9^{2-}, and $TISn_8^{3-}$ with the $2n + 2 = 20$ skeletal electrons required for an $n = 9$ vertex globally delocalized D_{3h} deltahedron analogous to $B_9H_9^{2-}$ and Bi_9^{5+} anomalously having 22 rather than the expected 20 skeletal electrons suggesting[3] incomplete overlap of the unique internal orbitals directed towards the core of the deltahedron.

Bicapped square antiprism. $TISn_9^{3-}$ with the $2n + 2 = 22$ skeletal electrons required for an $n = 10$ vertex globally delocalized D_{4d} deltahedron analogous to that found in the $B_{10}H_{10}^{2-}$ anion.

Gas Phase

The following gas phase post-transition metal clusters have been observed in the greatest abundances in the laser vaporization experiments using a supersonic molecular beam apparatus[10,11,12]:

Neutral bismuth clusters. Bi_4 with 12 skeletal electrons postulated to have a tetrahedral structure like P_4.

Cationic bismuth clusters. Bi_3^+ isoelectronic with the cyclopropenyl cation $C_3H_3^+$ and thus postulated to have an equilateral triangular structure; Bi_5^+ with 14 skeletal electrons isoelectronic with B_5H_9 and thus postulated to have a nido square pyramidal structure; Bi_7^+ with the requisite number of skeletal electrons for an edge-localized 7-vertex polyhedron having 11 edges, 6 faces, 6 vertices of degree 3, and one vertex of degree 4.

Anionic bismuth clusters. Bi_2^- and Bi_5^- isoelectronic with the paramagnetic NO and the cyclopentadienide anion, C_5H_5, respectively.

Tin and lead clusters. The neutral 2n apparent skeletal electron systems E_7 and E_{10} (E = Sn, Pb) postulated to have capped octahedron and 3,4,4,4-tetracapped trigonal prism structures, respectively, each having C_{3v} symmetry and one tetrahedral chamber.

Mixed post-transition metal clusters. Pb_5Sb_4 and Sn_5Bi_4 isoelectronic with Sn_9^{4-} and Bi_9^{5+} observed in condensed phases[16] and postulated to have a nido C_{4v} capped square antiprism structure analogous to Sn_9^{4-}; Pb_3Sb_2, Pb_4Sb_2, and Pb_5Sb_2 having 2n + 2 skeletal electrons and isoelectronic with the deltahedral carboranes $C_2B_3H_5$, $C_2B_4H_6$, and $C_2B_5H_7$ known[17] to have trigonal bipyramid, octahedron, and pentagonal bipyramid structures, respectively.

These examples suggest that principles of structure and bonding which are applicable to condensed phase metal clusters may also be applied to gas phase post-transition metal clusters arising from molecular beam experiments. However, further very difficult experimental work is needed on the gas phase post-transition metal clusters in order to obtain evidence confirming or disproving the structures postulated above.

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LITERATURE REFERENCES

1. R.B. King and D.H. Rouvray, J. Am. Chem. Soc. 99:7834 (1977).
2. R.B. King in: "Chemical Applications of Topology and Graph Theory," R.B. King, ed., Elsevier, Amsterdam (1983).
3. R.B. King, Inorg. Chim. Acta 57:79 (1982).
4. R.B. King, Inorg. Chim. Acta 116:99 (1986).
5. R.B. King in: "Mathematics and Computational Concepts in Chemistry," N. Trinajstić, ed., Ellis Horwood, Chichester (1986).
6. R.B. King, Inorg. Chim. Acta 116:109 (1986).
7. R.B. King, Inorg. Chim. Acta 116:119 (1986).
8. R.B. King, Inorg. Chim. Acta 116:125 (1986).
9. R.B. King, Int. J. Quantum Chem. in press.
10. R.G. Wheeler, K. LaiHing, W.L. Wilson, and M.A. Duncan, Chem. Phys. Lett., in press.
11. R.G. Wheeler, K. LaiHing, W.L. Wilson, J.D. Allen, R.B. King, and M.A. Duncan, submitted for publication.
12. M.E. Geusic, R.R. Freeman, and M.A. Duncan, submitted for publication.
13. T.G. Dietz, M.A. Duncan, D.E. Powers, and R.E. Smalley, J. Chem. Phys. 74:6511 (1981).
14. K. Ruedenberg, J. Chem. Phys. 22:1878 (1954).
15. H.H. Schmidtke, J. Chem. Phys. 45:3920 (1966).
16. J.D. Corbett, Chem. Rev. 85:383 (1985).
17. R.N. Grimes, "Carboranes," Academic Press, New York, N.Y. (1970).

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