Inorganica Chimica Acta, 144 (1988) 173–176

Cluster of Clusters (C^2) Model for Electron Counting of Supracluster Based on Smaller Cluster Units

BOON K. TEO* and HONG ZHANG

Department of Chemistry, University of Illinois at Chicago, Box 4348, Chicago, Ill. 60680, U.S.A.

(Received July 7, 1987)

Abstract

High nuclearity metal clusters are often based on vertex-, edge-, or face-sharing of small cluster units. Understanding of the bonding in these clusters in general, and their ligand requirements in particular, is a prerequisite to the design of even larger clusters. We describe here a new 'cluster of clusters' (C^2) model which is a simple but useful approach to electron counting of high nuclearity clusters based on smaller clusters as building blocks. Specifically, the C^2 model provides a simple means to calculate the number of skeletal as well as topological electron pairs of a supracluster based on its constituents (building blocks).

Introduction

High nuclearity metal clusters are often based on vertex-, edge-, or face-sharing of small cluster units. Recently we reported the synthesis and structure of a series of gold–silver–phosphine clusters based on vertex-sharing of centered icosahedral (13-atom) units [1]. For example, the structure of a 25-atom cluster containing 13 Au and 12 Ag atoms $[(Ph_3P)_{12}Au_{13}Ag_{12}Br_8]^+$ [1c] can be regarded as two Au-centered Au_7Ag_6 icosahedra sharing one Au-atom as a common vertex. Similarly, the 38-atom cluster $[(p\text{-}Tol_3P)_{10}Au_{18}Ag_{20}Cl_{14}]$ [1d] can be viewed as three Au_7Ag_6 centered icosahedra sharing three corners in a triangular arrangement with two more Ag atoms capping the top and the bottom Ag_3 triangles. It is apparent that these novel structural characteristics may open up new pathways to the design of even larger metal clusters via fusion of smaller cluster units as building blocks. We shall refer to this concept as 'cluster of clusters' and to the resulting clusters as 'superclusters'.

Understanding of the bonding in these supraclusters in general, and their ligand requirements in particular, is important in the design, syntheses, and structures of high nuclearity metal clusters. We wish to describe here a new electron counting scheme which grew out of our attempt to rationalize, as well as to predict, the electronic requirements of the Au–Ag supraclusters (based on vertex-sharing icosahedra) synthesized and structured in our laboratory. We shall refer to this electron counting approach as 'C^2(cluster of clusters)' model. It turns out that this new approach can also be applied to other cluster systems based on vertex-, edge-, or face-sharing of smaller cluster units as building blocks. There have been, of course, many bonding approaches [2, 3] or electron counting schemes [4, 5] available for polyhedral clusters. The method presented here, however, has the advantage of providing a simple way for predicting the total electron count, as well as for calculating the number of skeletal electron pairs for these 'cluster of clusters'. We shall show how one can calculate the number of skeletal electron pairs of a high nuclearity supracluster from its constituents.

'Cluster of Clusters' (C^2) Model

The C^2 model is based on an extension of the Topological Electron Counting (TEC) approach [6, 7] recently developed by us. In the spirit of the TEC rule [7], the number of 'skeletal electron pairs' can be given by

$$B = 3V - E \qquad \text{for 0-D and 1-D} \qquad (1a)$$

$$B = 2V - F + \epsilon + X \qquad \text{for 2-D and 3-D} \qquad (1b)$$

systems and the total number of electron pairs by

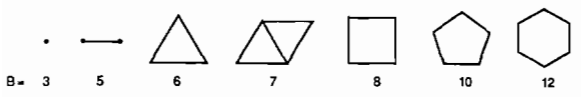
$$T = V_n + 6V_m + B \qquad (2)$$

where V is the number of vertices ($V = V_n + V_m$ where V_n and V_m represent the number of main-group and transition metal atoms, respectively), E is the number of edges, F is the number of faces, ϵ is the Euler characteristic ($\epsilon = D - 1$ where D is the dimensionality of the cluster). Note that both eqn. (1a) and (1b) stem from the assumption that each skeletal atom contributes three orbitals for cluster bonding [7]. Equation (1b) is derived from Euler's theorem, $E = V + F - \epsilon$. X is an 'adjustment' parameter [6, 7].

*Author to whom correspondence should be addressed.

0020-1693/88/$3.50

© Elsevier Sequoia/Printed in Switzerland



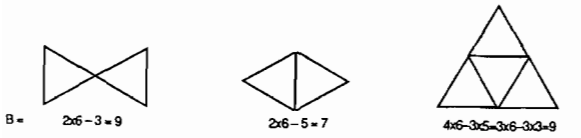
Scheme 1. B values for some 0-, 1-, 2-D systems.

Using eqn. (1), it is possible to calculate the skeletal electron pairs (B) associated with a specific cluster moiety, fragment, or cage. For example, the B values for some commonly observed polygons and polyhedra are given in Scheme 1. For 0-D and 1-D systems, $B = 3V - E$ (eqn. (1a) where E is the number of edges. Thus $B = 3 \times 1 - 0 = 3$ for a single atom and $B = 3 \times 2 - 1 = 5$ for a dimer. For the 2-D system in Scheme 1, we have, using eqn. (1b), $B = 2 \times 3 - 1 + 1 = 6$ for the triangle (Δ), $B = 2 \times 4 - 2 + 1 = 7$ for the rhombus, $B = 2 \times 4 - 1 + 1 = 8$ for the square ($\square$), $B = 2 \times 5 - 1 + 1 = 10$ for the pentagon ($\bigcirc$), etc.

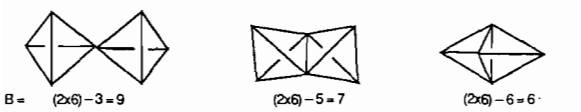
According to the C^2 model, for a supracluster which can be regarded as a cluster formed by n polyhedral clusters fused together, the B value is given by the sum of the B_j values ($j = 1$ to n) of the n individual cluster units minus the sum of the B_k values ($k = 1$ to s) of the s shared vertice(s), edge(s), of face(s)

$$B = \sum B_j - \sum B_k \qquad (3)$$

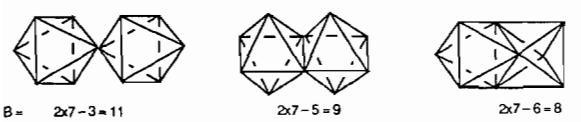
In other words, in order to obtain the overall or effective number of skeletal electron pairs (B) for a supracluster, we simply sum up the skeletal electron pairs (B_j) of the individual cluster units (building blocks) followed by subtracting the overcounting of the skeletal electron pairs (B_k) of the shared vertices, edges, or faces. Some examples of vertex-, edge-, and face-sharing supraclusters in 2-D, 3-D, or mixed 2-D and 3-D systems are depicted in Schemes 2–5. The total number of electron pairs (T) can be calculated from eqn. (2) and the total electron counts by $N = 2T$. We shall discuss some of these examples next.



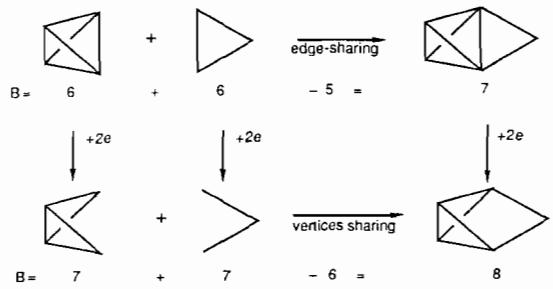
Scheme 2. 2-D Systems.



Scheme 3. 3-D Systems.



Scheme 4. 3-D Systems.



Scheme 5. Mixed-dimension systems.

Discussions

Let us consider, as depicted in Scheme 2, two triangles (Δ) sharing a vertex (left). Since each triangle has a B value of 6, and sharing a vertex diminishes the B value by 3 (*cf.* Scheme 1), we obtain a composite B value of $2 \times 6(\Delta) - 3(\text{atom}) = 9$. One example is $Os_5(CO)_{19}$ [8]. From eqn. (2) we predict $T = 39$ and $N = 78$. The observed electron count is $N_{obs} = 5 \times 8 + 19 \times 2 = 78$ which is in perfect agreement with the predicted N value. For two triangles sharing an edge which is shown in Scheme 2 (middle), eqn. (3) predicts $B = 2 \times 6(\Delta) - 5(\text{edge}) = 7$. One beautiful example is $Re_4(CO)_{16}^{2-}$ [9]. For this planar cluster, eqn. (2) predicts $T = 6 \times 4 + 7 = 31$ and $N = 62$ which is in perfect agreement with $N_{obs} = 4 \times 7 + 16 \times 2 + 2 = 62$.

The ν_2 triangle shown in Scheme 2 (right) can be considered either as three triangles sharing three corners ($B = 3 \times 6(\Delta) - 3 \times 3(\text{atom}) = 9$) or four triangles sharing three edges ($B = 4 \times 6(\Delta) - 3 \times 5(\text{edge}) = 9$). It is interesting to note that the two distinct descriptions give rise to the same B value. One novel example is the planar hexaosmium cluster $Os_6(CO)_{17}[P(OMe)_3]_4$ [10] with $N_{obs} = 6 \times 8 + 17 \times 2 + 4 \times 2 = 90$. The predicted values are: $T = 6 \times 6 + 9 = 45$, and also $N = 90$*.

As examples of fused polyhedra in 3-D, let us consider two tetrahedra (T_d) sharing a vertex (Scheme 3, left), an edge (middle), and a face (right). Since each tetrahedron contributes a B value of 6 (*cf.* eqn. (1b)), the C^2 model predicts a B value of $B = 2 \times 6(T_d) - 3(\text{atom}) = 9$, $2 \times 6(T_d) - 5(\text{edge}) = 7$, and $2 \times 6(T_d) - 6(\Delta) = 6$, respectively via eqn. (3). One example for two tetrahedra sharing a vertex is $Os_5S_2(CO)_{14}H_2$ [12] with five Os and two S atoms as vertices. The observed electron count is N_{obs} =

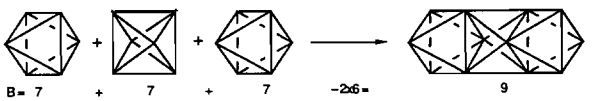
*It should be pointed out, however, that another commonly observed B value for ν_2 triangle is 6 as predicted by the Shell model [5]. According to the Shell model, $T = 6G + K = 6 \times 6 + 6 = 42$ and $N = 84$ where G is the total number of metal atoms and K is the B value at the center of the cluster (in this case $K = 6$ since the cluster centers at a triangular hole). One notable example is the $Cu_3Fe_3(CO)_{12}^{3-}$ trianion [11] with $N_{obs} = 3 \times 11 + 3 \times 8 + 12 \times 2 + 3 = 84$.

$5 \times 8 + 2 \times 6 + 14 \times 2 + 2 \times 1 = 82$. The predicted electron count is $N = 2T = 2 \times (V_n + 6V_m + B) = 2 \times (2 + 6 \times 5 + 9) = 2 \times 41 = 82$ (*cf.* eqn. (2)), in perfect agreement. Two tetrahedra sharing an edge is exemplified by $Mo_2Fe_2S_2(C_5H_5)_2(CO)_8$ [13] with $Mo_2Fe_2S_2$ as the cluster skeleton. The observed electron count is $N_{obs} = 2 \times 6 + 2 \times 8 + 2 \times 6 + 2 \times 5 + 8 \times 2 = 66$ which again agrees with the predicted electron count which is $N = 2 \times (2 + 6 \times 4 + 7) = 66$. Finally, two tetrahedra sharing a triangular face gives rise to a trigonal bipyramidal structure. One example is $Os_5(CO)_{16}$ [8] where $N_{obs} = 5 \times 8 + 16 \times 2 = 72$ agrees with the predicted electron count of $N = 2 \times (6 \times 5 + 6) = 72$. Trigonal bipyramids, however, can also be considered as a basic polyhedron such that other electron counting rules apply*.

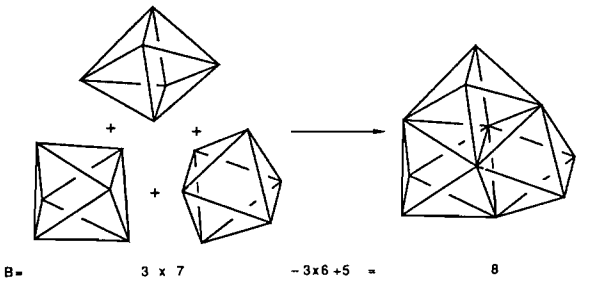
Similarly, since each octahedron (O_h) contributes a B value of 7 (*cf.* eqn. (1b)), two octahedra sharing a vertex (Scheme 4, left), an edge (middle), and a face (right) will give rise to the predicted B values of $B = 2 \times 7(O_h) - 3(\text{atom}) = 11$, $2 \times 7(O_h) - 5(\text{edge}) = 9$, and $2 \times 7(O_h) - 6(\Delta) = 8$, respectively. The latter two structures are exemplified by clusters $Ru_{10}C_2(CO)_{24}^{2-}$ [14], and $Rh_9(CO)_{19}^{3-}$ [15] with $N_{obs} = 10 \times 8 + 2 \times 4 + 24 \times 2 + 2 = 138$, and $9 \times 9 + 19 \times 2 + 3 = 122$ which agree reasonably well with the predicted electron counts of $N = 2 \times (6 \times 10 + 9) = 2 \times 69 = 138$, $2 \times (6 \times 9 + 8) = 124$ respectively.

In Scheme 5, we show an interesting sequence of cluster fusion in mixed dimensions. On the top we have a tetrahedron (3-D) sharing an edge with a triangle (2-D), giving rise to an edge-capped tetrahedron with $B = 6(T_d) + 6(\Delta) - 5(\text{edge}) = 7$. At the bottom is a 'butterfly' cluster (pseudo 2-D) sharing two vertices with a chain-like trimer (pseudo 1-D), giving rise to the so-called 'hinged butterfly'. The 'butterfly' can be considered as two triangles sharing an edge (*cf.* Scheme 2, middle), hence $B = 7$. For the pseudo chain of trimer, $B = 3V - E = 3 \times 3 - 2 = 7$. From eqn. (3), we obtain $B = 7 + 7 - 2 \times 3(\text{atom}) = 8$ for the 'hinged butterfly'. One important point to note in Scheme 5 is that each of the bottom clusters has one (and only one) electron pair over the corresponding top cluster. In other words, *electron counts are not necessarily additive in the condensation of clusters.* A beautiful example of the edge-capped tetrahedron is $Os_5H_2(CO)_{16}$ [8] with $N_{obs} = 5 \times 8 + 2 \times 1 + 16 \times 2 = 74$ which agrees well with the predicted electron count of $N = 2 \times (6 \times 5 + 7) = 74$. Hinged butterflies are exemplified by the highly interesting clusters $Ru_5C(CO)_{16}$ and the related $H_2Ru_5C(CO)_{15}$ [8], both with $N_{obs} = 76$ which agrees with the predicted $N = 2 \times (6 \times 5 + 8) = 76$.

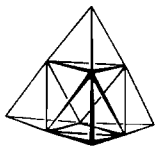
*In fact, many trigonal bipyramidal metal clusters are 76 ($B = 8$) rather than 72 ($B = 6$) electron systems (both of which are predicted by the TEC rule [6, 7]).



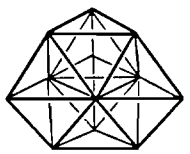
Scheme 6.



Scheme 7.



Scheme 8.



Scheme 9.

Besides providing some simple compounds for rationalizing the electron counts based on C^2 model illustrated in Schemes 2–5, some more complicated examples are shown in Schemes 6–9 which we shall discuss next.

Suppose we stack three octahedra together in a linear fashion such that they share two triangular faces, we obtain a face-sharing trioctahedron shown in Scheme 6. Here we predict $B = 3 \times 7(O_h) - 2 \times 6(\Delta) = 9$, in good agreement with that deduced from TEC rule. For a dodecavertex metal cluster, we predict $T = 6V_m + B = 6 \times 12 + 9 = 81$ (eqn. (2)) or an electron count of $N = 2T = 162$. This geometry, as well as the predicted electron count, has only recently been realized by the reported synthesis and structure of the $Ir_{12}(CO)_{26}^{2-}$ [16] dianion which has an electron count of $N_{obs} = 12 \times 9 + 26 \times 2 + 2 = 162$.

If, instead, we fuse three octahedra in a cyclic manner such that they share three faces, we obtain an undecavertex metal cluster with a 'hidden' bond as exemplified by the intriguing $[Rh_{11}(CO)_{23}]^{3-}$ [17] trianion shown in Scheme 7. Here each octahedron contributes a B value of 7, sharing three

triangular faces diminishes the B value by 6 each, and the hidden bond increases B by 5, resulting in a final B value of $3 \times 7(O_h) - 3 \times 6(\Delta) + 5(\text{hidden edge}) = 8$, and hence $T = 6 \times 11 + 8 = 74$ and $N = 2 \times 74 = 148$. The observed electron count is $N_{obs} = 11 \times 9 + 23 \times 2 + 3 = 148$, in perfect agreement with the predicted value.

Now, let us consider two higher nuclearity metal clusters. A decavertex metal cluster with a ν_2 tetrahedral structure (Scheme 8) is exemplified by the beautiful $[Os_{10}C(CO)_{24}]^{2-}$ [18] dianion. The metal framework can be considered as four tetrahedra sharing triangular faces with the central octahedron. Thus, $B = 4 \times 6(T_d) + 7(O_h) - 4 \times 6(\Delta) = 7$; $T = 6 \times 10 + 7 = 67$, and $N = 134$. The latter agrees well with $N_{obs} = 10 \times 10 + 4 + 24 \times 2 + 2 = 134$.

The truncated ν_2 trigonal bipyramid, shown in Scheme 9, can be considered as two octahedra sharing a face which is further fused with three trigonal bipyramids (tbp) via sharing of three rhombus ($B = 7$). If each trigonal bipyramid has $B = 8$*, we predict the overall $B = 2 \times 7(O_h) - 6(\Delta) + 3 \times 8(\text{tbp}) - 3 \times 7(\text{rhombus}) = 11$. This is indeed observed in $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ [19] where we predict an electron count of $N = 2 \times (6V_m + B) = 2 \times (6 \times 12 + 11) = 166$ which agrees well with the observed value of $N_{obs} = 12 \times 10 + 21 \times 2 + 4 = 166$.

Conclusions

In conclusion, the cluster of clusters (C^2) model presented here is a simple but useful approach to electron counting of high nuclearity clusters based on smaller clusters as building blocks. It enables us to calculate the number of skeletal electron pairs based on its consituents or building blocks (eqn. (3)). Combining with the TEC rule (eqn. (2)), the total number of electron pairs, and hence the overall electron count, can easily be calculated and compared with the experimental results.

Acknowledgements

Acknowledgement is made to the donors of the Petroleum Research Fund (No. 18873-AC3), administered by the A.C.S., for partial financial support of this research. B.K.T. is also grateful to the University of Illinois at Chicago for a Campus Research Board Award and a start-up fund in partial support of this research.

*See footnote on p. 175.

References

1 (a) B. K. Teo and K. Keating, *J. Am. Chem. Soc, 106*, 2224 (1984); (b) B. K. Teo, M. Hong, H. Zhang and D. Huang, *Angew. Chem., Int. Ed. Engl., 26*, 897 (1987); (c) for publication; (d) B. K. Teo, M. Hong, H. Zhang, D. Huang and X. Shi, *J. Chem. Soc., Chem. Commun.*, accepted for publication; *Chem. Eng. News, 65*, 21 (1987).
2 (a) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys., 36*, 2179 (1962); (b) R. E. Williams, *Inorg. Chem., 10*, 210 (1971); (c) K. Wade, *J. Chem. Soc., Chem. Commun.*, 792 (1971); *Adv. Inorg. Chem. Radiochem., 18*, 1 (1976); (d) D. M. P. Mingos, *Acc. Chem. Res., 17*, 311 (1984); (e) A. Sone, *Inorg. Chem., 20*, 563 (1981).
3 (a) J. W. Lauher, *J. Am. Chem. Soc., 100*, 5305 (1978). (b) *101*, 2604 (1979); (c) J. W. Lauher, *J. Organomet. Chem., 213*, 25 (1981).
4 (a) R. B. King, *Inorg. Chim. Acta, 116*, 99 (1986); (b) *116*, 109 (1986); (c) *116*, 119 (1986); (d) *116*, 125 (1986); (e) R. B. King and D. H. Rouvray, *J. Am. Chem. Soc., 99*, 7834 (1977).
5 (a) B. K. Teo and N. J. A. Sloane, *Inorg. Chem., 24*, 4545 (1985); (b) N. J. A. Sloane and B. K. Teo, *J. Chem. Phys., 83*, 6520 (1985); (c) B. K. Teo and N. J. A. Sloane, *Inorg. Chem., 25*, 2315 (1986).
6 (a) B. K. Teo, *Inorg. Chem., 23*, 1251 (1984); (b) B. K. Teo, G. Longoni and F. R. K. Chung, *Inorg. Chem., 23*, 1257 (1984).
7 (a) B. K. Teo, *Inorg. Chem., 24*, 1627 (1985); (b) B. K. Teo, *Inorg. Chem., 24*, 4209 (1985).
8 B. F. G. Johnson, *Philos. Trans. R. Soc. London., Ser. A, 308*, 5 (1982).
9 M. R. Churchill and R. Bau, *Inorg. Chem., 7*, 2606 (1968).
10 R. J. Goudsmit, B. F. G. Johnson, J. Lewis, P. R. Raithby and K. Whitmire, *J. Chem. Soc., Chem. Commun.*, 640 (1982).
11 G. Doyle, K. A. Eriksen and D. Van Engen, *J. Am. Chem. Soc., 107*, 7914 (1985).
12 R. D. Adams, Z. Dawoodi, D. F. Forest and B. E. Segmuller, *J. Am. Chem. Soc., 105*, 831 (1983).
13 P. D. Williams, M. D. Curtis, D. N. Duffey and W. M. Butler, *Organometallics, 2*, 165 (1983).
14 C. M. T. Hayward, J. R. Shapley, M. R. Churchill, C. Bueno and A. L. Rheingold, *J. Am. Chem. Soc., 104*, 7347 (1982).
15 S. Martinengo, A. Fumagalli, R. Bonfichi, G. Ciani and A. Sironi, *J. Chem. Soc., Chem. Commun.*, 825 (1982).
16 R. D. Pergola, F. Demartin, L. Garlaschelli, M. Manassero, S. Martinengo and M. Sansoni, *Inorg. Chem., 26*, 3487 (1987).
17 A. Fumagalli, S. Martinengo, G. Ciani and A. Sironi, *J. Chem. Soc., Chem. Commun.*, 453 (1983).
18 P. F. Jackson, B. F. G. Johnson, J. Lewis, W. J. H. Nelson and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 2099 (1982).
19 R. W. Broach, L. F. Dahl, G. Longoni, P. Chini, A. J. Schultz and J. M. Williams, *Adv. Chem. Ser., No. 167*, 93 (1978).