Theoretical Analyses and Electron Counting Rules for High Nuclearity Clusters

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The bonding in high nuclearity clusters with close packed arrangements of metal atoms is dependent primarily on the radial interactions between the surface and interstitial atoms; these clusters are characterised by $12n_s + \Delta_i$ valence electrons, where n_s is the number of surface atoms and Δ_i is a characteristic of the interstitial group of atoms.

As metal carbonyl cluster chemistry has evolved an important and fundamental relationship between the observed metal polyhedral geometry and the total number of valence electrons has been discovered.[1] Initially this relationship was limited to deltahedral and three-connected polyhedral molecules,[2,3] but has subsequently been extended to four-connected[4] and condensed clusters.[5] The theoretical basis of these electron counting rules is now well understood as a result of molecular orbital calculations on specific molecules,[6] the isolobal principle,[7] and Stone's Tensor Surface Harmonic Theory.[8] The extension of these bonding principles to really high nuclearity clusters with 15—50 metal atoms is an important prerequisite for understanding the relationship between molecular clusters and the bulk metal.[9]

The structures of high nuclearity clusters arise from the vertex, edge, and face sharing of smaller polyhedral units. When the degree of condensation is limited, the relationship between the observed structures and the polyhedral moieties from which they were derived is transparent and the condensation electron counting rules[1,5] are applicable. When the degree of condensation is extensive the observed structures

are more conveniently described in terms of those close packed arrangements which are characteristic either of the bulk metal or of crystallites of the metal. The bonding in such clusters is not readily described in terms of the condensation rules and is the subject of the bonding analysis presented below. Extensive condensation of tetrahedral and octahedral clusters leads to packing arrangements which are related to body centred cubic (b.c.c.), hexagonal (h.c.p.), and cubic (c.c.p.) metallic arrangements. The observed structures of metal clusters with 13—44 metal atoms (see Tables 1—3) can be described in terms of these packing arrangements or composites of them, *e.g.* f.c.c. and b.c.c. In addition close packed arrangements with fivefold symmetry are possible for molecular species and these are described in the Tables as icosahedral close packed (i.c.p.). The known clusters have between 1 and 6 interstitial (n_i) and between 12 and 38 surface metal atoms (n_s). This paper develops a simple relationship between n_i, n_s, and the total number of valence electrons in high nuclearity clusters.

Molecular orbital analyses on high nuclearity gold clusters $[Au\{Au(PR_3)\}_{n_s}]^{x+}$ have demonstrated that they are charac-

Table 1.. Examples of high nuclearity cluster compounds where radial bonding interactions predominate.

Compound	Ref.	n_i	n_s	Structure	Electron count		
					Obs.	Calc.	
$[Au_9(PPh_3)_8]^+$	10a	1	8	b.c.c.	114	114 ⎫	
$[Au_{11}I_3(PPh_3)_7]$	10b	1	10	b.c.c./i.c.p.	138	138 ⎬	$12n_s + 18$
$[Au_{13}Cl_2(PMePh_2)_{10}]^{3+}$	10c	1	12	i.c.p.	162	162 ⎭	
$[Pt_{19}(CO)_{22}]^{4-}$	10d	2	17	i.c.p.	238	238 ⎫	$12n_s + 34$
$[Rh_{22}(CO)_{35}H_{5-q-m}]^{q-}$	10e	2	20	f.c.c./b.c.c.	273+m	274 ⎭	
$[Au_{13}Ag_{12}Cl_6(PPh_3)_{12}]^{m+}$	10f	3	22	i.c.p.	317−m	314	$12n_s + 50^a$
$[Pt_{26}(CO)_{32}]^{2-}$	10g	3	23	h.c.p.	326	324 (326)	$12n_s + 48(50)^b$
$[Ni_{38}Pt_6(CO)_{48}H_{6-n}]^{n-}$	10h	6	38	f.c.c.	542	542 ⎫	$12n_s + 86^c$
$[Pt_{38}(CO)_{44}H_m]^{2-}$	10g	6	32	f.c.c.	470 + m	470 ⎭	

[a] Linear M_3 interstitial moiety. [b] Triangular M_3 interstitial moiety. Although isolated M_3 clusters are characterised by 48 valence electrons, the presence of bridging metal atoms can lead to the stabilisation of an a_2' M.O. and a valence electron count of 50 (D. G. Evans and D. M. P. Mingos, *Organometallics*, 1983, **2**, 435). [c] Octahedral M^6 moiety.

Table 2. Examples of high nuclearity clusters where radial and tangential effects are important.[a]

Compound	Ref.	n_i	n_s	Structure	Electron count		
					Obs.	Calc.	
$[Rh_{13}(CO)_{24}H_5]$	10i	1	12	h.c.p. anti-cuboctahedron	170	170 ⎫	
$[Rh_{15}(CO)_{30}]^{3-}$	10j	1	14	b.c.c. deltahedron	198	198	
With non-metal interstitial atoms							$12n_s + (2n_s +2)$
$[Ru_6C(CO)_{17}]$	1	1	6	octahedron	86	86	
$[Rh_{10}S(CO)_{22}]^{2-}$	1	1	10	bicapped square-antiprism	142	142	
$[Rh_{12}Sb(CO)_{27}]^{3-}$	1	1	12	icosahedron	170	170 ⎭	

[a] The clusters summarised in this Table have either deltahedral or four-connected polyhedral geometries. *Nido-* and *arachno*-clusters derived from them have electron counts of $14n_s + 4$ and $14n_s + 6$ respectively (ref. 2). Condensed clusters derived from these polyhedra have electron counts governed by the condensation rules given in refs. 1 and 5.

Table 3. Examples of high nuclearity clusters where the tangential bonding interactions make a partial contribution.

Compound	Ref.	n_i	n_s	Structure	Electron count		
					Obs.	Calc.	
$[Rh_{14}(CO)_{25}]^{4-}$	10k	1	13	b.c.c.	180	180 ⎫	
$[Rh_{14}(CO)_{26}]^{2-}$	10l	1	13	b.c.c.	180	180	
$[Rh_{15}(CO)_{27}]^{3-}$	10m	1	14	b.c.c./h.c.p.	192	192 ⎬	$12n_s + 24$
$[Rh_{17}(CO)_{30}]^{3-}$	10n	1	16	h.c.p.	216	216	
$[Rh_{22}(CO)_{37}]^{4-}$	10o	1	21	f.c.c./h.c.p.	276	276	
$[Pt_{24}(CO)_{30}]^{2-}$	10g	1	23	f.c.c.	302	300 ⎭	

terised by $12n_s + 18$ valence electrons for alternative body centred and icosahedral metal geometries (see Table 1).[10,11] In these clusters the radial metal–metal bonding effects predominate and result in the formation of four, S^σ and P^σ, molecular orbitals between the 6s orbitals of the surface atoms and the 6s and 6p orbitals of the central atom. The filled d orbitals of the central atom interact only weakly with the D_s^σ and D_p^σ functions of the surface atoms and complete the 18 electron contribution to the total electron count. The ligands give rise to a set of n_s bonding orbitals localised mainly on the ligands and create matching antibonding orbitals from the radial metal 6p orbitals. These when taken with the filled d shells of the surface gold atoms contribute to the $12n_s$ component. In these clusters the surface metal atoms are functioning in a manner akin to ligands in co-ordination compounds which conform to the 18 electron rule. Extension of this model to clusters with several interstitial atoms suggests

an electron count of $12n_s + \Delta_i$, where Δ_i reflects the electronic requirements of the interstitial moiety as defined below:

(n_i)	Δ_i	Molecular analogue
1	18	$Mo(CO)_6$
2	34	$Mn_2(CO)_{10}$
3 (triangular)	48	$Os_3(CO)_{12}$
3 (linear)	50	$OsRe_2(CO)_{14}$
4 (tetrahedral)	60	$Ir_4(CO)_{12}$
6 (octahedron)	86	$Rh_6(CO)_{16}$

Examples of clusters which conform to this generalisation are summarised in Table 1.[10] Given the extreme complexity of these systems the agreement between observed and calculated electron counts is remarkably good even for the highest

nuclearity cluster with 44 metal atoms. Some of the compounds given in Table 1 have been incompletely characterised and the generalisation provides a basis for estimating either the number of hydrides or the charge on the cluster. Interestingly the observed electron count is rather insensitive to the mode of packing, a result which is consistent with the observed soft potential energy surface for clusters where radial bonding predominates[11] and the bulk metal where it is known that only small energy differences separate the alternative structures.[12]

In the examples cited in Table 1 the bonding approximates to the radial model developed for gold clusters, because the number of bridging ligands is insufficient to introduce surface functions which do not match the filled molecular orbitals localised predominantly on the interstitial atoms. When the number of carbonyl ligands is equal to or greater than twice the number of surface atoms the bridging carbonyl ligands create linear combinations which match those of the L^{π} functions, derived from the p orbitals of the surface atoms. The metal p orbitals are too high lying to make a significant contribution to bonding in the absence of bridging ligands. The resultant molecular orbitals are localized predominantly on the carbonyls but in symmetry terms emulate the in-phase p orbital combinations of the surface metal atoms. Molecular orbital calculations on this type of cluster[13] have suggested the occurrence of a filled d shell on the central atom, S^{σ} and P^{σ} radial bonding molecular orbitals and $(n-8)L^{\pi}$ (L = 3,4) tangential functions localised mainly on the carbonyl ligands. This leads to an electron count of $12n_s + 18 + 2(n_s - 8) = 14n_s + 2$. This is identical to the electron counts established for deltahedral and four-connected metal clusters, which have either main group interstitial atoms or no interstitial atoms.[1,8] Examples of such clusters are given in Table 2. $[Rh_{13}(CO)_{24}H_5]$ has an anti-cuboctahedral geometry which can be alternatively described as a fragment of h.c.p. and $[Rh_{15}(CO)_{30}]^{3-}$ has a deltahedral geometry which can be described also as a fragment of b.c.c.

When the bridging-carbonyl-to-surface-atom ratio falls between these two extremes, i.e. lies between 1.3 and 2.0, then not all the L^{π} functions are generated. Remarkably an inspection of the known clusters demonstrates that in general three of the F^{π} functions are utilised in bonding and electron counts of $12n_s + 24$ are observed for five of the six known examples. In $[Pt_{24}(CO)_{30}]^{2-}$ an additional electron pair is accommodated in these surface molecular orbitals. The compounds given in Table 3 also do not show a strong stereochemical preference and adopt all three of the packing types common to bulk metals. This conclusion is at variance with a proposal that the structures of high nuclearity clusters can be distinguished on the basis of the total number of valence electrons.[9]

The model developed above has several important implications for cluster chemistry and the transition from molecular to bulk properties. The observation that even these high nuclearity clusters conform to simple electron counting rules suggests that they are attaining stable closed shell electronic configurations. This behaviour is different from that anticipated for crystallites and the bulk transition metals which are electronically unsaturated.[11] As the nuclearity of the cluster increases it is apparent that the close link between cluster stereochemistry and the total number of valence electrons is lost. This is consistent with a transition to the bulk metal properties where only small energy differences separate the alternative structures.[12]

The description of the electronic structures of the compounds given in the Tables is consistent with a primary involvement of the metal d and s orbitals in metal–metal bonding with little contribution from the metal p orbitals. Woolley has also noted the antibonding character of the metal p orbital interactions in clusters and the metal.[14] Although for formal electron counting purposes it appears that the d shells are filled and make no net contribution to bonding in the clusters, back donation effects involving the carbonyls preferentially depopulate the antibonding sections of the 'd band' in molecular clusters and strengthen the metal–metal bonding effects.

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