A Simple Electron Counting Rule for Close-packed High Nuclearity Metal Clusters

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A simple electron counting rule based on an extended Hume–Rothery rule has been developed for close-packed high nuclearity metal clusters.

Recently there has been considerable interest in large close-packed metal cluster compounds (*cf.* Table 1)[1–10] with metal arrangements resembling fragments of metallic lattices. We report here a simple electron counting rule (based on an extended Hume–Rothery rule[11]) for correlating and/or predicting the metal packing arrangements in these high nuclearity metal clusters.

For a metal cluster with m_b 'bulk' atoms and m_s 'surface' atoms (the nuclearity is $m = m_b + m_s$), the total number of electrons N (including valence electrons from the metals and

Table 1. The packing type, the numbers of bulk (m_b) and surface (m_s) atoms, the numbers of electrons per bulk (n_b) and surface (n_s) atoms, and the calculated ($N_{calc.}$) and observed ($N_{obs.}$) electron counts for a number of close-packed high nuclearity metal clusters.

No.	Cluster	Packing	m_b	m_s	n_b	n_s	$N_{calc.}$	$N_{obs.}$	% error[a]
(**1**)	$[Rh_{13}(CO)_{24}H_{5-q}]^{q-}$ (q = 2,[e] 3,[f] 4[g])	hcp[b]	1	12	11.75	13.22	170.4	170	0
(**2**)	$[Rh_{14}(CO)_{25}H_{4-q}]^{q-}$ (q = 3,[h] 4[i]) $[Rh_{14}(CO)_{26}]^{2-}$ [j]	Incomplete bcc[c]	1	13	11.50	12.94	179.7	180	0
(**3**)[k]	$[Rh_{15}(CO)_{27}]^{3-}$	bcc/hcp	1	14	11.50	12.94	192.6	192	0
(**4**)[l]	$[Rh_{15}(CO)_{30}]^{3-}$	bcc	1	14	11.50	12.94	192.6	198	−3
(**5**)[m]	$[Rh_{17}(CO)_{30}]^{3-}$	hcp	1	16	11.75	13.22	223.3	216	3
					11.24	12.64	213.5	216	1
(**6**)[n]	$[Rh_{22}(CO)_{37}]^{4-}$	fcc/hcp	1	21	11.24	12.64	276.7	276	0
(**7**)[o]	$[Rh_{22}(CO)_{35}H_{5-q+x}]^{q-}$ (q = 4, 5)	fcc/bcc	2	20	11.24	12.64	275.3	273+x	—
(**8**)[p]	$[Pt_{19}(CO)_{22}]^{4-}$	Pentagonal	2	17	11.17	12.56	235.9	238	−1
(**9**)[r]	$[Pt_{24}(CO)_{30}]^{2-}$	fcc[d]	1	23	11.24	12.64	301.9	302	0
(**10**)[r]	$[Pt_{26}(CO)_{32}]^{2-}$	hcp	3	23	11.75	13.22	339.3	326	4
					11.24	12.64	324.4	326	0
(**11**)[r]	$[Pt_{38}(CO)_{44}H_2]^{2-}$	fcc	6	32	11.24	12.64	471.9	472	0
(**12**)[s]	$[Au_{13}(PMe_2Ph)_{10}Cl_2]^{3+}$	Icosahedral	1	12	11.17	12.56	161.9	162	0

[a] % error = 100 × ($N_{calc.}$ − $N_{obs.}$)/$N_{obs.}$ [b] Hexagonal close-packed. [c] Body-centred cubic. [d] Face-centred cubic. [e] Ref. 1a. [f] Ref. 1b. [g] Ref. 1c. [h] Ref. 2a. [i] Ref. 2b, c. [j] Ref. 2d. [k] Ref. 3. [l] Ref. 4. [m] Ref. 5. [n] Ref. 6. [o] Ref. 7. [p] Ref. 8. [r] Ref. 9. [s] Ref. 10.

electrons donated by the ligands) is given by $N = m_b n_b + m_s n_s$ where n_b and n_s are the numbers of electrons per bulk and surface atoms, respectively. Let $n_b = n$ and $n_s = rn$, then N can be rewritten as in equation (1), where $r = n_s/n_b$ is the ratio

$$N = (m_b + rm_s)n \qquad (1)$$

of the numbers of valence electrons residing on the surface *vs.* the bulk atoms. To determine the ratio r as well as the number n, we extend the Hume–Rothery (HR) rule[11] for the composition of intermetallic compounds to metal cluster systems. The HR rule states that certain alloy structures occur at a definite electron/atom ratio (*viz.*, sum of valence electrons/sum of ionic atoms): the β (body-centred cubic, bcc), γ (complicated cubic structure), and ϵ (hexagonal close packed, hcp) phases inevitably occur at the ratios 21/14, 21/13, and 21/12, as exemplified by CuZn, Cu_5Zn_8, and $CuZn_3$, respectively. Also observed is the α (face-centred cubic, fcc) phase of Cu_3Zn at the ratio of 5/4. Including the d shell, the number of valence electrons per *bulk* atom can be approximated by n = 10 + 21/18 = 11.17 for pentagonal; 10 + 21/17 = 11.24 for fcc; 10 + 21/14 = 11.50 for bcc; 10 + 21/13 = 11.62 for γ (complicated cubic structure); and 10 + 21/12 = 11.75 for hcp structures. Using these n values for the known structures shown in Table 1 [excluding (**4**), (**5**), (**7**), (**8**), and (**10**)], we determine an average r value of 1.124 ± 0.003. Note that r *is basically a constant which is independent of the structures.* Since r is close to the ratio 18/16, we choose to use r = 1.125. Equation (1) then provides a way of partitioning the total number of electrons N among the m_b bulk and m_s surface atoms. The results are given in Table 1 for a number of known clusters. For example, the $[Pt_{38}(CO)_{44}H_2]^{2-}$ dianion[9] has a fcc packing with 6 'bulk' atoms (an octahedron) and 32 'surface' atoms (a truncated octahedron of frequency three). Using n = 11.24 (fcc) and r = 1.125, we calculated N = 471.9 from equation (1), in excellent agreement with the observed electron count of N = 38 × 10 + 44 × 2 + 2 × 1 + 2 = 472. Several points need to be emphasized. Firstly, though one n value is specified for each packing structure, some variation is to be expected (in analogy to alloy phases). Thus, the n value for pentagonal packing could range from 11 to 11.25; for the fcc (α) structure from 11.00 to 11.38; for the bcc (β) structure from 11.48 to 11.50; for the γ structure from 11.58 to 11.66; and for the hcp (ϵ) structure from 11.72 to 11.78. For metal clusters with approximately hcp structures, it is evident from Table 1 that the n value can either be 11.75 [for (**1**)] or 11.25 [for (**5**) and (**10**)]. The latter is possible for relatively small clusters (one bulk atom) with hcp structures because the difference in electronic requirements or energetics between hcp and fcc is very small. Secondly, for mixed structures, *e.g.* fcc/hcp for the $[Rh_{22}(CO)_{37}]^{4-}$ cluster,[6] often the lower n values are observed. Finally, the calculated electron counts agree with the observed values to better than 1% accuracy for all except (**4**) where the six capping metal atoms are farther away from the centre atom than predicted by an ideal bcc packing, thereby accounting for the extra electrons.

It is interesting to note from Table 1 that the number of electrons per bulk atom is $11 \leqslant n_b \leqslant 12$ whereas that per surface atom n_s is always greater than 12. The former is consistent with close-packed structures commonly adopted by late transition metals (note that five d and one s valence orbitals can accommodate a maximum of 12 electrons) owing to the repulsion between the full or nearly full d shells of adjacent atoms. The latter reflects the participation of p orbitals of surface atoms capable of accepting electrons from the ligands. The average n value can indicate the type (surface *vs.* bulk) of metal atoms present in a cluster. For example, the tetrahedral[12] $Ir_4(CO)_{12}$ (60e), octahedral[13] $Rh_6(CO)_{16}$ (86e), cubic[14] $Ni_8(PPh)_6(CO)_8$ (120e), ν_2 tetrahedral (or tetracapped octahedral)[15] $[Os_{10}C(CO)_{24}]^{2-}$ (134e), and the truncated ν_2 trigonal bipyramidal (hcp layers of 3:6:3)[16] $[Ni_{12}(CO)_{21}H_{4-q}]^{q-}$ where q = 2,3,4 (166e) clusters have n values of 15, 14.33, 15, 13.4, and 13.83 electrons per metal atom, respectively, all indicative of only the existence of surface atoms, whereas the average n values for (**1**)—(**12**) is <*ca.* 13.

The rather narrow range of the n values for each type of packing may, under favourable conditions, allow differentiation and/or prediction of the most symmetrical structures for clusters of a given nuclearity. Another utility of the electron counting rule presented here is to predict the number of hydrides present in a cluster (which is sometimes difficult to determine experimentally). For example, our rule predicts that the $[Rh_{22}(CO)_{35}H_{5-q+x}]^{q-}$ (q = 4, 5)[7] clusters, which have a mixed cubic close-packed and bcc structure, should have 275 electrons. The observed value is (273 + x) from which x = 2 can be deduced.

The theoretical basis for the proposed electron counting theory for close-packed high nuclearity metal clusters is as follows. Since it is known that the density of states for a metal cluster quickly approaches that of the band structure of the bulk as the cluster size increases, it may be reasonably assumed that the Brillouin zones of the various packing structures can be used to approximate the density of states of discrete metal clusters when the cluster size reaches a critical size and shape/symmetry. We take this critical size as one with at least one *completely encapsulated* bulk atom since it has been shown that all of the major features of the bulk density of states are present in the density of states of such cluster.[17] As the cluster size increases, this approximation should improve (*cf.* Table 1). The Brillouin zones for various crystal packing structures are well known. The inscribed sphere of the first zone for fcc, bcc, γ, and hcp structures should theoretically contain up to (including the d orbibals) 11.36, 11.48, 11.54, and 11.75 electrons per bulk atom.[18] With the exception of pentagonal close-packed structures which are not possible in a three-dimensional crystal lattice, these values are indeed very close to the n values specified above for each type of structure. For hexagonally packed structures, the theoretical n value depends also on the c/a ratio (lattice dimensions).

In conclusion, this paper presents a simple electron counting rule for large close-packed metal clusters in the same spirit as the well established Hume-Rothery rule for intermetallic compounds. It is striking to find that the electronic requirements predicted by band structure theory for metals or metallic alloys, which are characterized by long-range order, can be extended to discrete metal clusters where only short-range order is important. Nevertheless, the electron counting rule proposed here is consistent with the recent theoretical results that the density of states of a metal cluster rapidly converges to that of the bulk metal even at the aggregation of 13 (fcc) to 15 (bcc) atoms.[17] It should, however, be cautioned that metal cluster compounds stabilized by ligands have chemical and physical properties very different from those of *bare* metal particles.

The author is indebted to Drs. G. Longoni and S. Martinengo (Istituto di Chimica Generale dell'Universitá e Centro del CNR, Milan, Italy) for numerous discussions on high nuclearity metal clusters as well as Drs. H. S. Chen and C. Y. Kuo (Bell Labs, Murray Hill) for helpful discussions on band theory.

Received, 8th August 1983; Com. 1068

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