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The Cluster Valence Electrons (VE) Are Natural Numbers of Clusters Generated by K(N) Parameters: VE and K(N) Are Intertwined

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Abstract

The paper presents a highly refined work on broad categorization of clusters using the series method with emphasis on cluster valence content. In this regard, the K(n) parameter plays a crucial role. The K(n) parameters are interrelated and have been utilized to generate a cluster map of clusters. The cluster map of skeletal elements and their clusters can be extended indefinitely. The elements refer to main group and transition metal elements. The inter-conversion of K(n) parameter map into a selected portion of cluster valence electron content map was done indicating the origin of the cluster valence electron numbers which are sometimes associated with certain characteristic geometries. The map indicates that the main group and transition metal elements and their clusters are all interlinked via either the K(n) map or the cluster valence electron content map.

Keywords: cluster valence, broad categorization, K(n) parameter, cluster map, skeletal numbers

1. Introduction

The polyhedral skeletal electron pair theory (PSEPT) has been exceedingly helpful in analyzing chemical clusters for a very long time (Welch,2013;Wade,1971, 1976;Mingos,1972,1984a,1984b) and the electron counting is very important in this analysis (Tolmann,1972; Jemmis, et al,2001a,Jemmis,2001b, 2003,2005,2008; Jemmis, 2003,2008; Wales,2005;Vajenine&Hoffmann,1998;Mingos,1991;Teo,et al,1984;Rossi& Zanello,2011).Relatively recently, a strong desire arose to see whether or not the simple and complex carbonyl clusters were interrelated. The study began with the analysis of osmium carbonyl clusters. It was found that the osmium carbonyl clusters follow the series S =14n+q (Kiremire, 2014, 2015a-e). This relationship was found to be true for other transition metal carbonyl clusters (Kiremire, 2016a-e). Furthermore ,it was also discovered that the main group clusters such as boranes follow the series S = 4n+q where q = 0,2,4, 6,8,and so on for uncapping clusters while the capping clusters follow the series with q = 0 -2,-4,-6,-8, and so on (Kiremire,2015f). It was later generalized that the categorization of clusters could be easily done using the simpler series formula S =4n+q for both transition metals and main group clusters (Kiremire, 2016a). The use of the series method resulted into the discovery of skeletal numbers which have been found to be versatile and useful in analyzing clusters (Kiremire, 2016c, 2017a-d). Using skeletal numbers, the K(n) parameters of molecules and clusters have been calculated(Kiremire,2017a-d). The skeletal numbers of elements which are used in calculating K(n) parameters of molecules and clusters are provided in the Appendix table. The skeletal numbers of ligands are assigned from the knowledge of series simply by giving a vector of K= -0.5 for every electron donated by the ligand to the cluster. Thus, a [：CO] ligand which donates 2 electrons has a K value of -1, while a Cp ligand which donates 5 electrons has a K value of -2.5.

2. Results and Discussion

2.1 Information Derived from the K(n) Parameter

Some of the vital information the K(n) parameter contains was extensively covered in earlier work(Kiremire,2018a,2018b). Among others, it includes organizing CLUSTERS into CLANS as illustrated in Figure 1, and FAMILIES of clusters as indicated in Figures 2-6 and predicting the shapes of clusters. Deeper analysis of the K(n) values of clusters revealed that the values can be regarded as unifying agents of chemical clusters. The K(n) parameter brings together the clusters with the same skeletal number, K and the same number of skeletal elements,(n) which belong to the same cluster series S = 4n+q. Such clusters may be regarded as being members of the same FAMILY. Selected examples of clusters which belong to the same families are given in Figures 2-6. Furthermore, a cluster family has a tendency of adopting identical geometries or isomer configurations. For instance, Figure 2 shows a cluster family with K(n) = 8(5). This family is characterized by 5 skeletal elements and 8 cluster linkages. These clusters usually adopt

an ideal SQUARE PYRAMIDAL SHAPE, C_{4v}. They belong to the series S = 4n+4(Nido family). Their cluster valence electron content is given by Ve* = 14n+4 where n =5 and hence Ve =14(5)+4 = 74 for transition metal clusters. On the other hand, the cluster family K(n) = 6(4) normally represents clusters with an ideal TETRAHEDRAL shape, T_d. These clusters belong to the family series S = 4n+4 with the cluster valence electron content Ve = 14n+4 = 14(4)+4 = 60. The scheme for deriving the series S = 4n+q from K(n) was discussed earlier(Kiremire, 2017d). Since, the use of the series method is relatively new, it can be summarized in Scheme 1.

*In this paper, the symbol (Ve) has been used for cluster valence electrons for simplicity instead of CVE generally found in literat.ure.

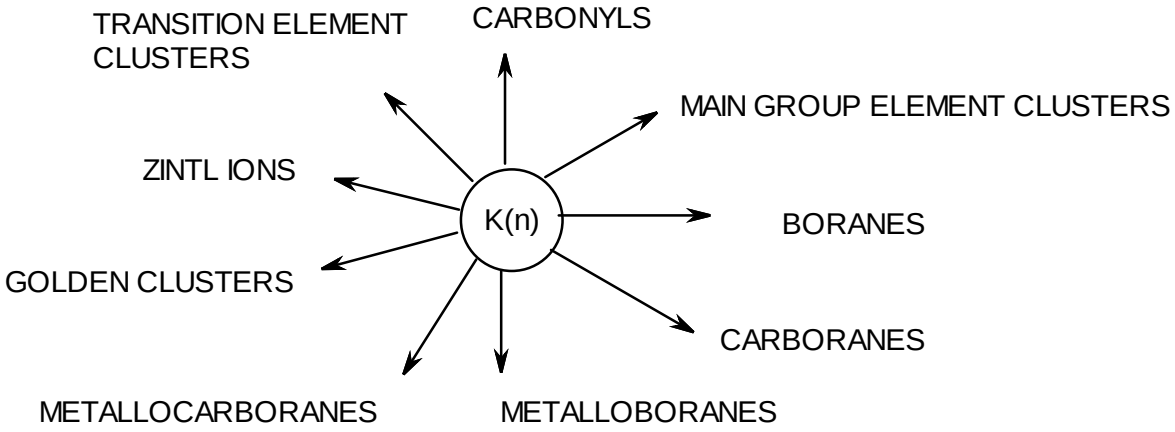


Figure 1. Illustration of unifying power of K(n) parameter for selected cluster groups

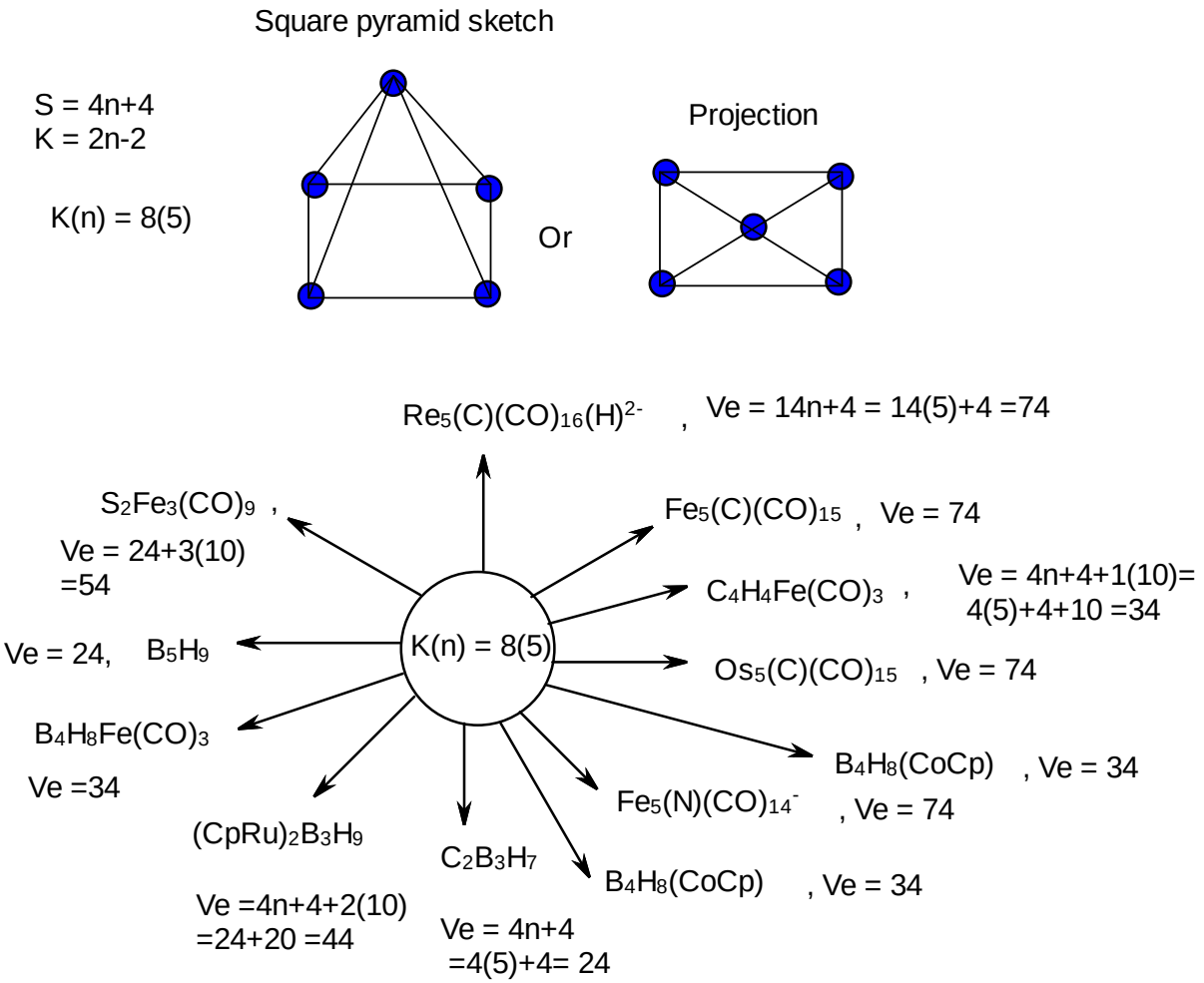


Figure 2. Illustration of selected cluster family members with square pyramid skeletal shape

K(n) = 6(4); S =4n+4, K =2n-2, Ve =14n+4 =14(4)+4 = 60 for TM
Ve = 4n+4 = 4(4)+4 = 20 for MG: TM = Transition metal, MG = Main group elements

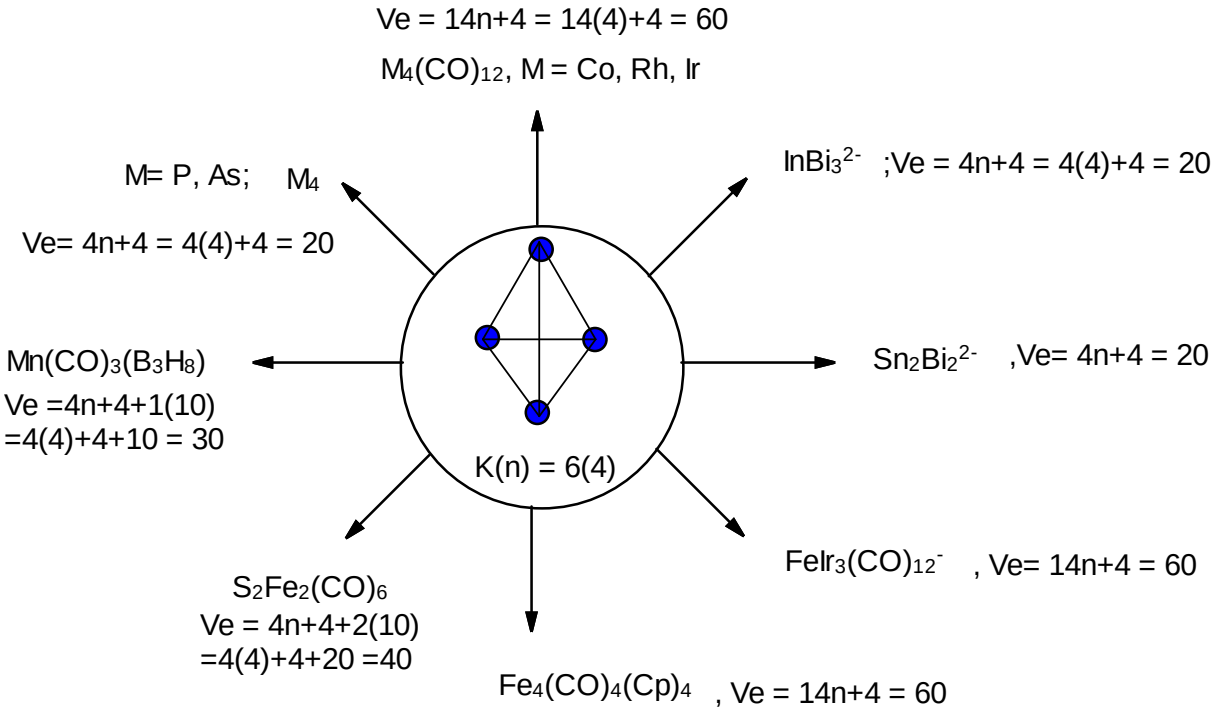


Figure 3. Selected family members of clusters with tetrahedral skeletal shape

K(n) = 1(2); S =4n+6, K =2n-3, Ve = 14n+6 = 14(2)+6 = 34, TM
Ve = 4n+6 = 4(2)+6 = 14, MG
TM = Transition metal, MG = Main group element

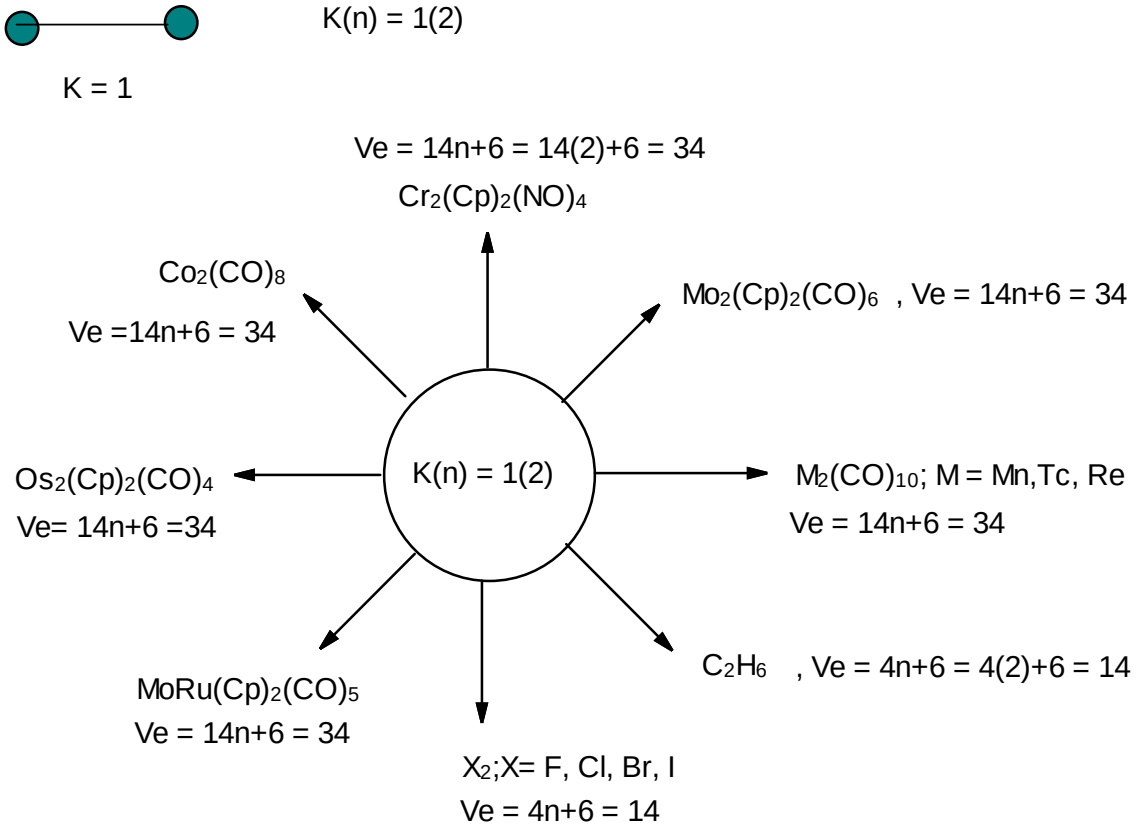


Figure 4. Selected cluster family members with one bond linking two skeletal elements

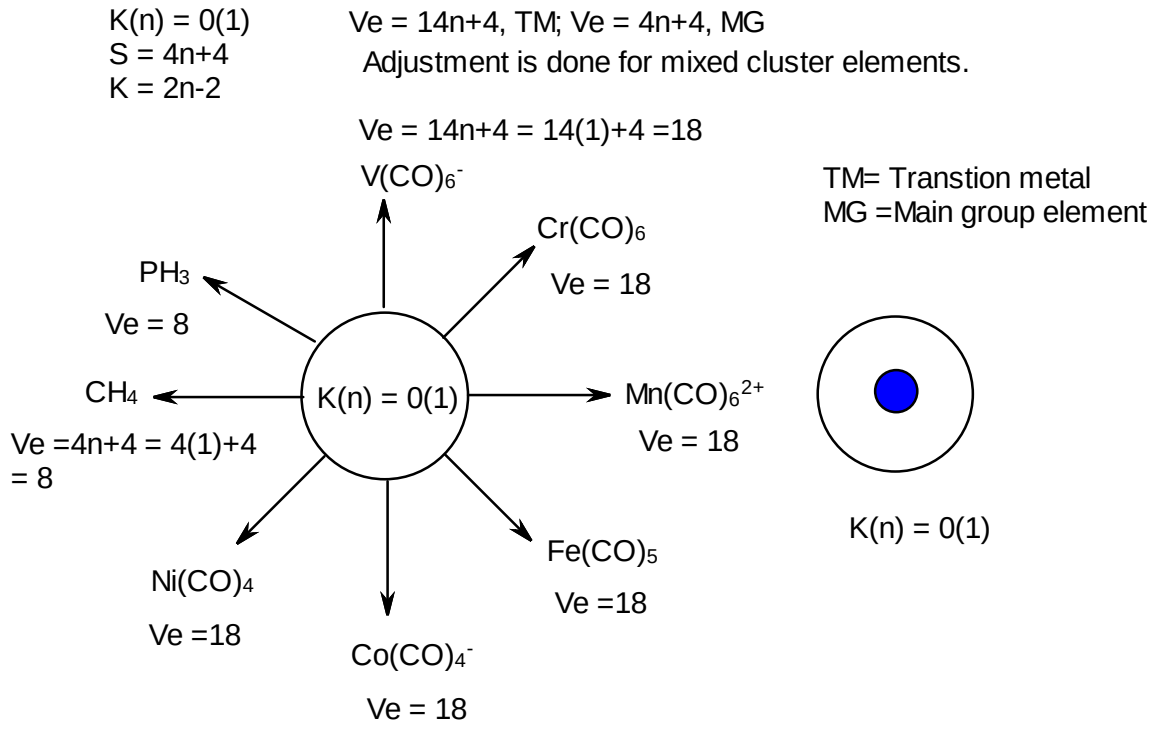


Figure 5. Cluster members which obey either octet or 18 electron rule

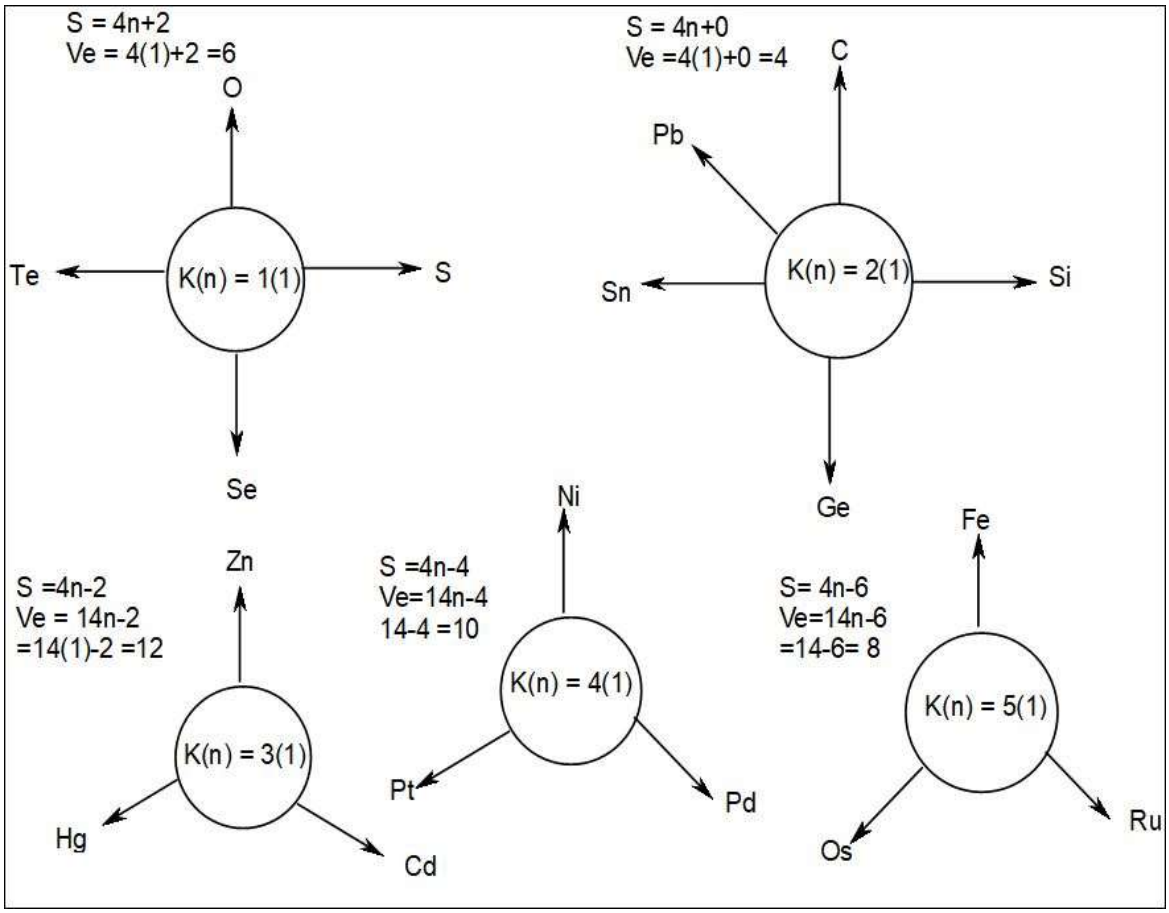
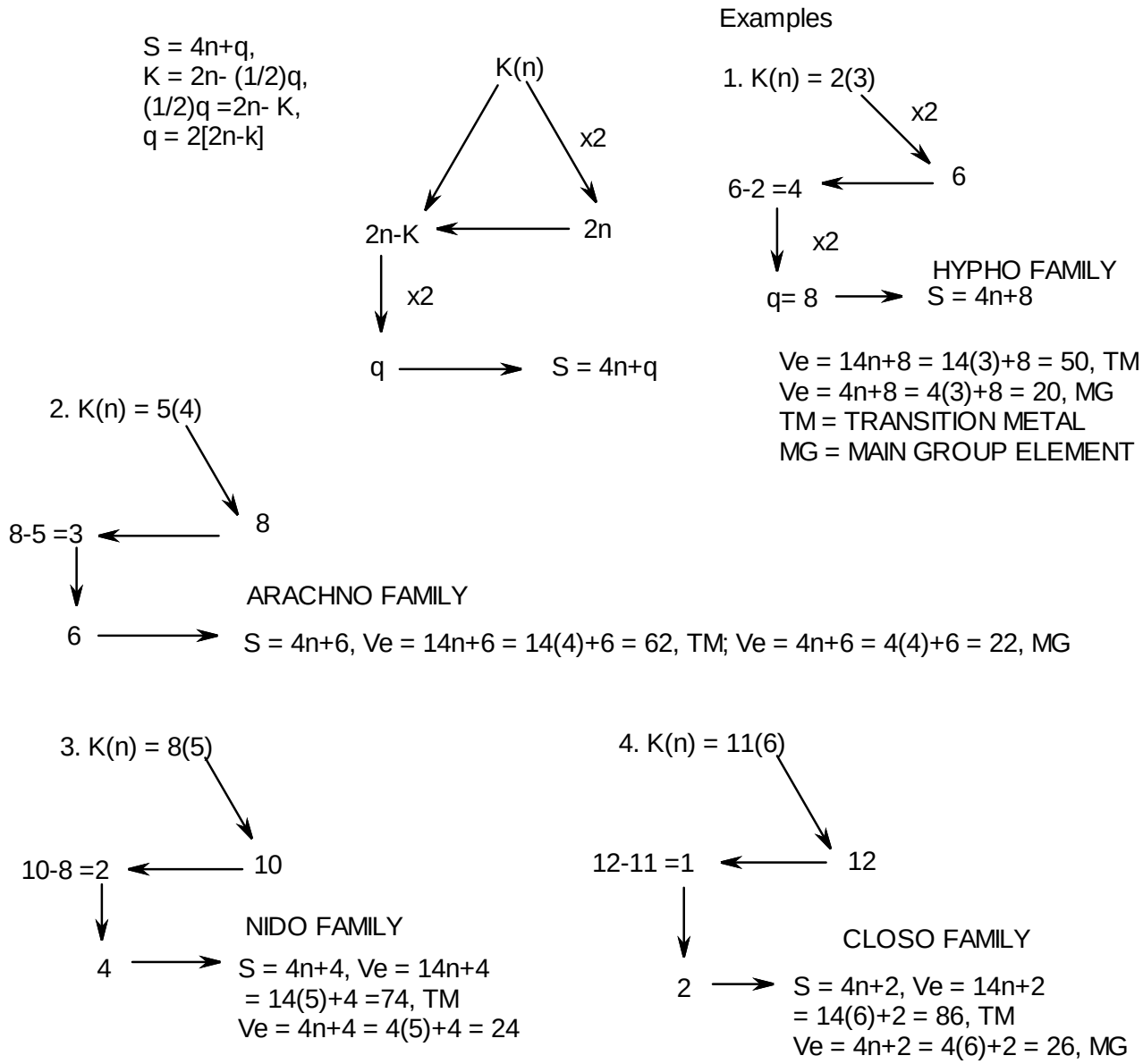


Figure 6. Illustrations of skeletal numbers linking up naked skeletal elements



Scheme1. Selected examples illustrating the simple method of deriving the series formula

2.2 The Cluster Valence Electrons and the Periodic Map of Skeletal Elements and Clusters

The cluster valence electrons of transition metal complexes are usually cited by many books and articles (Fehlner & Harlet, 2007; Housecroft & Sharpe, 2005; Mingos, 1984; Teo, et al, 1984; Wheeler & Hoffmann, 1986). In this paper, a fundamental principle that the cluster valence electrons are a direct consequence of K(n) parameter will be demonstrated. This is amply illustrated by the simple calculations in Table 1 for transition metal and main group clusters. The calculations also clearly show the powerful predictive nature of the cluster valence electron content by the K(n) parameter. The valence electron content of a cluster is precisely numerically the same as calculated from its respective K(n) parameter. The parameter behaves as if it were a car park designated for a particular make of cars. Such clusters may be considered to constitute a family of clusters. This point will be discussed further under broad categorization of clusters. Recent publications put emphasis on the cluster valence electron content of most clusters studied (Zanello, 2002; Rossi & Zanello, 2011). A selected sample of clusters from the publications have been analyzed for their valence electron contents and categorized. These are given in Table 2. The K(n) parameters are interrelated and portray a map of a matrix of chemical clusters. Portion of the map that covers some of the K(n) values of the clusters selected is given in Table 3. The table has been constructed in such a way as to cover some of the clusters and elements presented in this paper. The mapped K(n) values are highlighted in Table 3. Also the section of clusters such as boranes studied by Rudolph (Rudolph, 1976) are highlighted. Due to the significance of the information the table contains, it has been

reproduced in several varied ways (Kiremire, 2015d, 2017a). Among the important information the K(n) parameter subtly conveys is the cluster valence electron content. For instance, K(n) = 9(5), S = 4n+2, Ve =14n+2;and since n = 5, Ve = 14(5)+2 = 72. The interpretation in this case is that the parameter represents an ideal trigonal bipyramid shape and the cluster will have a valence electron content of 72. For the purposes of illustrating the concept of cluster valence electron content, a portion of Table 3 has been extracted and converted into valence electron content and is shown in Table 4. Very important information on cluster valence electron content can be picked from Table 4. For instance, when Nx =1, V = 18 represents all the mono-skeletal clusters which obey the famous 18 electron rule, while the slot of Ve = 16 which represents all mono-skeletal clusters which obey the 16 electron rule. The mono-skeletal clusters which obey the 16 and 18 electron rules play significant roles in catalysis (Tolman, 1972). In order to demonstrate what the Table 4 means, let us take a specific example, $Fe(CO)_5$. This cluster from Nx =1 column, obeys the 18 electron rule, hence, Ve = 18. When a CO ligand is added, we get a hypothetical cluster, $Fe(CO)_6$(Ve=20), further addition of a CO ligand, we generate the species, $Fe(CO)_7$(Ve=22) . The next process produces, the cluster, $Fe(CO)_8$(Ve = 24), and so on. But if we reverse the process and remove a CO ligand beginning with $Fe(CO)_5$ cluster, we generate successive fragments, $Fe(CO)_4$(Ve= 16), $Fe(CO)_3$(Ve=14), $Fe(CO)_2$(Ve=12), $Fe(CO)_1$(Ve=10), Fe(Ve=8), Fe^{2+}(Ve = 6) and so on. Mono-skeletal complexes with cluster valence electron contents,$TiCl_4$(Ve=8), MeAuL(L=PR_3,Ve=14), $RhHL_3$(Ve=16),Cp_2TiCl_2(Ve=16), and $Ni(H_2O)_6^{2+}$(Ve=20) are known. Similar considerations can be extended to other columns. In other words, the columns represent nuclearity cluster trees discussed in previous publications (Kiremire, 2017e, 2018a).

The clusters with nuclearity index of 3, that is, Nx = 3, with Ve = 48 include complexes such as $M_3(CO)_{12}$(M = Fe, Ru, Os) with triangular skeletal shape. We can also pick out Ve = 64, K=4, n = 4 which have a square skeletal shape; Ve = 62, K= 5 with a butterfly skeletal shape; n = 4; Ve = 60, K = 6 and n = 4 with a tetrahedral shape; Ve = 72, K = 9, n = 5, with a trigonal bipyramid; Ve = 86, K =11, n = 6 with an octahedral geometry; Ve = 84, K = 12, n=6, having a mono-capped trigonal bipyramid shape; and Ve = 90, K = 9, n = 6, with a trigonal prism shape. From Table 4 we can also readily identify the diagonal capping series of $\Delta K = 3$, $\Delta n = 0$ some of which are shown in Table 5. For example, Ve = 76 corresponds to Kp = C^5C[M1], Ve = 100→Kp = C^7C[M1]; and for [M2], Ve = 126→ C^8C[M2], and Ve= 162→Kp = $C^{11}C$[M2]. The valence electron content figures indicated in Table 4 refer to the clusters of transition metals. The corresponding sets of valence electron contents for main group elements clusters were calculated and put in arrays portrayed in Table 6. The cluster valence electron contents and their corresponding K(n) parameters of selected main group element clusters shown in Table 7 are well marked in blue in Table 6**.** A guide to determine the number of the number of cluster linkages is illustrated in Scheme2.The first step is to identify a valence electron content whose K(n) value is known. On the basis of the K(n) array in Table 3, any horizontal movement means an increase of K by 2.

But, a movement diagonally will give rise to an increase in K value by 3 while for he movement downwards, the K(n) parameter changes only by1. The selected hypothetical capping series based upon [M6] nucleus are shown in Scheme 3.

Table 1. Selected K(n) parameters and their derived cluster valence electron content

K(n)	SERIES, S= 4n+q	K=2n- ½ q	Kp =C^yC[Mx]*	Ve =14n+q	EXAMPLES	Ve =4n+q	EXAMPLES
1(2)	4n+6	2n-3	$C^{-2}C$[M4] =7-2(3) =1	14(2)+6 = 34	$Re_2(Cp)_2(CO)_5$(34), $M_2(CO)_8$, M=Co, Rh, Ir(34)	4(2)+6 =14	C_2H_6, F_2, Cl_2(14)
2(2)	4n+4	2n-2	$C^{-1}C$[M3] =5-1(3) =2	14(2)+4 = 32	$Re_2H_2(CO)_8$(32), $Rh_2(Cp)_2(CO)_2$(32)	4(2)+4 =12	O_2, C_2H_4, B_2H_6(12)
3(2)	4n+2	2n-1	C^0C[M2] =3-0(3)=3	14(2)+4 = 30	$Mo_2(Cp)_2(CO)_4$(30)	4(2)+2 =10	N_2, CO, NO^+, CN^-(10)
2(3)	4n+8	2n-4	$C^{-3}C$[M6] =11-3(3)=2	14(3)+8 = 50	$Os_3(CO)_{12}Cl_2$(50), $Re_3H_2(CO)_{13}^-$(50)	4(3)+8 =20	C_3H_8(20)
3(3)	4n+6	2n-3	$C^{-2}C$[M5] =9-2(3) =3	14(3)+6 = 48	$M_3(CO)_{12}$ M=Fe, Ru, Os(48), $Re_3(H)(CO)_{12}^{2-}$(48)	4(3)+6 =18	C_3H_6, O_3(18)
4(4)	4n+8	2n-4	$C^{-3}C$[M7] =13-3(3)=4	14(4)+8 = 64	$Os_4(CO)_{16}$(64), $Re_4H_4(CO)_{15}^{2-}$(64)	4(4)+8 = 24	C_4H_8(24)
5(4)	4n+6	2n-3	$C^{-2}C$[M6] =11-2(3)=5	14(4)+6 = 62	$Os_4(CO)_{15}$(62), $Re_4(CO)_{16}^{2-}$(62)	4(4)+6= 22	B_4H_{10}, C_4H_6(22)
6(4)	4n+4	2n-2	$C^{-1}C$[M5] =9-1(3) = 6	14(4)+4 = 60	$Os_4(CO)_{14}$(60), $Rh_4(CO)_{12}$(60), $Fe_4(Cp)_4(CO)_4$(60)	4(4)+4 = 20	P_4,B_4H_8, $InBi_3^{2-}$, $Sn_2Bi_2^{2-}$(20)
7(5)	4n+6	2n-3	$C^{-2}C$[M7]	14(5)+6 = 76	$Rh_5(CO)_{15}^-$(76)	4(5)+6 = 26	B_5H_{11}(26)
8(5)	4n+4	2n-2	$C^{-1}C$[M6]	14(5)+4=74	$Os_5(C)(CO)_{15}$(74)	4(5)+4=24	$C_2B_3H_7$(24)
9(5)	4n+2	2n-1	C^0C[M5]	14(5)+2=72	$Os_5(CO)_{16}$(72)	4(5)+2=22	Bi_5^{3+}(22)
6(6)	4n+12	2n-6	$C^{-5}C$[M11]	14(6)+12=96	$H_5Re_6(CO)_{24}^-$(96)	4(6)+12=36	C_6H_{12}(36)
10(6)	4n+4	2n-2	$C^{-1}C$[M7]	14(6)+4=88	$Re_6H_8(CO)_{18}^{2-}$(88)	4(6)+4=28	B_6H_{10}(28)
11(6)	4n+2	2n-1	C^0C[M6]	14(6)+2=86	$Rh_6(CO)_{16}$(86)	4(6)+2=26	$B_6H_6^{2-}$(26)
12(6)	4n+0	2n+0	C^1C[M5]	14(6)+0=84	$Os_6(CO)_{18}$(84)	4(6)+0=24 24+2(10)=44	$(Cp^*Re)_2B_4H_8$(44),
13(7)	4n+2	2n-1	C^0C[M7]	14(7)+2=100	$Co_7(N)(CO)_{15}^{2-}$(100)	4(7)+2=30	$B_7H_7^{2-}$(30)
14(7)	4n+0	2n+0	C^1C[M6]	14(7)+0=98	$Os_7(CO)_{21}$(98)	4(7)+0=28	
12(8)	4n+8	2n-4	$C^{-3}C$[M11]	14(8)+8=120	$Ni_8(PPh)_6(CO)_8$	4(8)+8 =40	Si_8R_8(40)
15(8)	4n+2	2n-1	C^0C[M8]	14(8)+2=114	$Cu_2Rh_6(C)(CO)_{15}L_2$(114)	4(8)+2=34	$B_8H_8^{2-}$(34)
17(8)	4n-2	2n+1	C^2C[M6]	14(8)-2=110	$Re_8(C)(CO)_{24}^{2-}$(110)	4(8)-2=30	
20(9)	4n-4	2n+2	C^3C[M6]	14(9)-4=122	$Rh_9(CO)_{19}^{3-}$(122)	4(9)-4=32	
25(9)	4n-14	2n+7	C^8C[M1]	14(9)-14=112	$Au_9L_8^{3+}$(112)	4(9)-14=22	
19(10)	4n+2	2n-1	C^0C[M10]	14(10)+2=142		4(10)+2=42	$B_{10}H_{10}^{2-}$(42)
23(10)	4n-6	2n+3	C^4C[M6]	14(10)-6=134	$Rh_{10}(CO)_{21}^{2-}$(134)	4(10)-6=34	
21(11)	4n+2	2n-1	C^0C[M11]	14(11)+2=156		4(11)+2=46	$B_{11}H_{11}^{2-}$(46)
26(11)	4n-8	2n+4	C^5C[M6]	14(11)-8=146		4(11)-8=36	
31(11)	4n-18	2n+9	$C^{10}C$[M1]	14(11)-18=136		4(11)-18=26	
23(12)	4n+2	2n-1	C^0C[M12]	14(12)+2=170		4(12)+2=50	$B_{12}H_{12}^{2-}$(50)
33(12)	4n-18	2n+9	$C^{10}C$[M2]	14(12)-18=150	$Au_{12}L_{10}Cl^{3+}$(150)	4(12)+2=50	
36(13)	4n-20	2n+10	$C^{11}C$[M2]	14(13)-20=162	$Au_{13}L_{10}Cl_2^{3+}$(162)	4(13)-20=32	

*Note that according to series, the nuclear [Mx] fragment follows the closo series S =4n+2 and K = 2n-1. Hence, K[Mx] = 2x-1.

Table 2. Comparison of cluster valence electrons calculated from series method with those of selected clusters from literature

CLUSTER	K(n)	S =4n+q	K	Kp=$C^{y}C$[Mx]	Ve =14n+q	Ve=18n-2K	Lit.*
$Pt_{19}(CO)_{22}^{4-}$	52(19)	4n-28	2n+14	$C^{15}C$[M4]	238	238	230
$Fe_4(C)(CO)_{13}$	5(4)	4n+6	2n-3	$C^{-2}C$[M6]	62	62	62
$Fe_4(C)(CO)_{12}^{2-}$	5(4)	4n+6	2n-3	$C^{-2}C$[M6]	62	62	62
$Fe_4(N)(CO)_{12}^{-}$	5(4)	4n+6	2n-3	$C^{-2}C$[M6]	62	62	62
$Fe_5(C)(CO)_{14}^{2-}$	8(5)	4n+4	2n-2	$C^{-1}C$[M6]	74	74	74
$Fe_5(C)(CO)_{15}$	8(5)	4n+4	2n-2	$C^{-1}C$[M6]	74	74	74
$Os_5(C)(CO)_{14}^{2-}$	8(5)	4n+4	2n-2	$C^{-1}C$[M6]	74	74	74
$Os_5(C)(CO)_{15}$	8(5)	4n+4	2n-2	$C^{-1}C$[M6]	74	74	74
$Fe_6(C)(CO)_{16}^{2-}$	11(6)	4n+2	2n-1	$C^{0}C$[M6]	86	86	86
$Fe_6(N)(CO)_{16}^{-}$	11(6)	4n+2	2n-1	$C^{0}C$[M6]	86	86	86
$Fe_3Rh_3(C)(CO)_{15}^{-}$	11(6)	4n+2	2n-1	$C^{0}C$[M6]	86	86	86
$Rh_6(C)(CO)_{13}^{2-}$	11(6)	4n+2	2n-1	$C^{0}C$[M6]	86	86	86
$Fe_3Pt_3(CO)_{15}^{2-}$	11(6)	4n+2	2n-1	$C^{0}C$[M6]	86	86	86
$Re_7(C)(CO)_{21}^{3-}$	14(7)	4n+0	2n+0	$C^{1}C$[M6]	98	98	98
$Ru_{10}(C)(CO)_{24}^{2-}$	23(10)	4n-6	2n+3	$C^{4}C$[M6]	134	134	134
$Ir_{12}(CO)_{24}^{2-}$	29(12)	4n-10	2n+5	$C^{6}C$[M6]	158	158	158
$Ru_6Pd_6(CO)_{24}^{2-}$	29(12)	4n-10	2n+5	$C^{6}C$[M6]	158	158	158
$Pt_{24}(CO)_{30}^{2-}$	65(24)	4n-34	2n+17	$C^{18}C$[M6]	302	302	302
$Pt_{38}(CO)_{44}^{2-}$	107(38)	4n-62	2n+31	$C^{32}C$[M6]	470	470	470
$Fe_4Au(CO)_{16}^{-}$	7(5)	4n+6	2n-3	$C^{-2}C$[M7]	76	76	76
$Rh_7(N)(CO)_{15}^{2-}$	13(7)	4n+2	2n-1	$C^{0}C$[M7]	100	100	100
$Co_7(N)(CO)_{15}^{2-}$	13(7)	4n+2	2n-1	$C^{0}C$[M7]	100	100	100
$Os_{18}Pd_3(C_2)(CO)_{42}^{2-}$	55(21)	4n-26	2n+13	$C^{14}C$[M7]	268	268	268
$Os_6(P)(CO)_{18}^{-}$	9(6)	4n+6	2n-3	$C^{-2}C$[M8]	90	90	90
$Os_6(P)(CO)_{18}^{3-}$	8(6)	4n+8	2n-4	$C^{-3}C$[M9]	92	92	92
$Fe_8(P)(CO)_{22}^{-}$	15(8)	4n+2	2n-1	$C^{0}C$[M8]	114	114	114
$Co_8(C)(CO)_{18}^{2-}$	15(8)	4n+2	2n-1	$C^{0}C$[M8]	114	114	114
$Rh_8(C)(CO)_{19}$	15(8)	4n+2	2n-1	$C^{0}C$[M8]	114	114	114
$Ru_{10}(C)_2(CO)_{24}^{2-}$	21(10)	4n-2	2n+1	$C^{2}C$[M8]	138	138	138
$Co_3Ni_7(C)_2(CO)_{15}^{3-}$	21(10)	4n-2	2n+1	$C^{2}C$[M8]	138	138	138
$PtRh_{10}(N)(CO)_{21}^{3-}$	24(11)	4n-4	2n+2	$C^{3}C$[M8]	150	150	150
$Ni_{12}(C)_2(CO)_{16}^{2-}$	27(12)	4n-6	2n+3	$C^{4}C$[M8]	162	162	164
$Co_{10}(P)(CO)_{21}^{3-}$	20(10)	4n+0	2n+0	$C^{1}C$[M9]	14(10)+0=140	140	142
$Rh_{14}(N)_2(CO)_{25}^{2-}$	32(14)	4n-8	2n+4	$C^{5}C$[M9]	188	188	188
$Co_9(P)(CO)_{21}^{2-}$	16(9)	4n+4	2n-2	$C^{-1}C$[M10]	14(9)+4=130	130	130
$Rh_9(P)(CO)_{21}^{2-}$	16(9)	4n+4	2n-2	$C^{-1}C$[M10]	130	130	130
$Co_{10}Rh(N)_2(CO)_{21}^{3-}$	22(11)	4n+0	2n+0	$C^{1}C$[M10]	154	154	154
$Co_{11}(C)_2(CO)_{22}^{3-}$	22(11)	4n+0	2n+0	$C^{1}C$[M10]	154	154	154
$Rh_{12}(C)_2(CO)_{24}^{2-}$	25(12)	4n-2	2n+1	$C^{2}C$[M10]	166	166	166
$Co_{13}(N)_2(CO)_{24}^{3-}$	28(13)	4n-4	2n+2	$C^{3}C$[M10]	178	178	178
$Co_{14}(N)_3(CO)_{26}^{3-}$	31(14)	4n-6	2n+3	$C^{4}C$[M10]	190	190	196
$Fe_6Ni_6(N)_2(CO)_{24}^{2-}$	24(12)	4n+0	2n+0	$C^{1}C$[M11]	168	168	168
$Rh_{12}(N)_2H(CO)_{23}^{3-}$	24(12)	4n+0	2n+0	$C^{1}C$[M11]	168	168	168
$Rh_{28}(N)_4H_2(CO)_{41}^{4-}$	72(28)	4n-32	2n+16	$C^{17}C$[M11]	360	360	360
$Co_8Pt_4(C_2)(CO)_{24}^{2-}$	23(12)	4n+2	2n-1	$C^{0}C$[M12]	170	170	170
$Rh_{14}(C)_2(CO)_{33}^{2-}$	25(14)	4n+6	2n-3	$C^{-2}C$[M16]	202	202	202
$Ni_{38}(H)(C)_6(CO)_{42}^{5-}$	95(38)	4n-38	2n+19	$C^{20}C$[M18]	494	494	456
$Co_{10}(N)_2(CO)_{29}^{4-}$	9(10)	4n+22	2n-11	$C^{-10}C$[M20]	162	162	142

*See Zanello in references

Table 3. A map of selected K(n) cluster parameters

	n	1	2	3	4	5	6	7	8	9	10	11	12	13	14
4n+26	2n-13							**1(7)**	**3(8)**	**5(9)**	**7(10)**	**9(11)**	**11(12)**	13(13)	15(14)
4n+24	2n-12	**RU**						**2(7)**	**4(8)**	**6(9)**	**8(10)**	**10(11)**	**12(12)**	14(13)	**16(14)**
4n+22	2n-11	**DO**					**1(6)**	**3(7)**	**5(8)**	**7(9)**	**9(10)**	**11(11)**	**13(12)**	**15(13)**	17(14)
4n+20	2n-10	**LP**				**0(5)**	**2(6)**	**4(7)**	**6(8)**	**8(9)**	**10(10)**	**12(11)**	**14(12)**	16(13)	18(14)
4n+18	2n-9	**H**				**1(5)**	**3(6)**	**5(7)**	**7(8)**	**9(9)**	11(10)	**13(11)**	**15(12)**	17(13)	19(14)
4n+16	2n-8	**SY**			**0(4)**	**2(5)**	**4(6)**	**6(7)**	**8(8)**	**10(9)**	**12(10)**	**14(11)**	**16(12)**	18(13)	20(14)
4n+14	2n-7	**ST**			**1(4)**	**3(5)**	**5(6)**	**7(7)**	**9(8)**	**11(9)**	**13(10)**	**15(11)**	**17(12)**	19(13)	21(14)
4n+12	2n-6	**EM**		**0(3)**	**2(4)**	**4(5)**	**6(6)**	**8(7)**	**10(8)**	**12(9)**	**14(10)**	**16(11)**	**18(12)**	20(13)	22(14)
4n+10	2n-5			**1(3)**	**3(4)**	**5(5)**	**7(6)**	**9(7)**	**11(8)**	**13(9)**	**15(10)**	**17(11)**	**19(12)**	21(13)	23(14)
4n+8	2n-4		**0(2)**	**2(3)**	**4(4)**	**6(5)**	**8(6)**	**10(7)**	**12(8)**	**14(9)**	**16(10)**	**18(11)**	**20(12)**	22(13)	24(14)
4n+6	2n-3		**1(2)**	**3(3)**	5(4)	**7(5)**	**9(6)**	**11(7)**	13(8)	**15(9)**	**17(10)**	**19(11)**	**21(12)**	23(13)	25(14)
4n+4	2n-2	**0(1)**	**2(2)**	**4(3)**	**6(4)**	8(5)	**10(6)**	**12(7)**	**14(8)**	**16(9)**	**18(10)**	**20(11)**	**22(12)**	24(13)	26(14)
4n+2	**2n-1**	**1(1)** [M1]	**3(2)** [M2]	**5(3)** [M3]	**7(4)** [M4]	**9(5)** [M5]	**11(6)** [M6]	**13(7)** [M7]	**15(8)** [M8]	**17(9)** [M9]	**19(10)** [M10]	**21(11)** [M11]	**23(12)** [M12]	25(13) [M1]	27(14) [M14]
4n+0	2n+0	**2(1)**	**4(2)**	**6(3)**	**8(4)**	**10(5)**	**12(6)**	**14(7)**	16**(8)**	18**(9)**	20**(10)**	**22(11)**	**24(12)**	26(13)	28(14)
4n-2	2n+1	**3(1)**	5**(2)**	**7(3)**	**9(4)**	**11(5)**	13(6)	15(7)	**17(8)**	19(9)	21(10)	23(11)	25(12)	**27(13)**	29(14)
4n-4	2n+2	**4(1)**	**6(2)**	8(3)	**10(4)**	**12(5)**	**14(6)**	16**(7)**	**18(8)**	**20(9)**	**22(10)**	24**(11)**	**26(12)**	**28(13)**	30(14)
4n-6	2n+3	**5(1)**	7(2)	9(3)	11(4)	**13(5)**	**15(6)**	17(7)	19(8)	21(9)	**23(10)**	**25(11)**	**27(12)**	29(13)	31(14)
4n-8	2n+4	**6(1)**	**8(2)**	10(3)	12(4)	14(5)	**16(6)**	**18(7)**	**20(8)**	22(9)	24(10)	**26(11)**	**28(12)**	30(13)	32(14)
4n-10	2n+5	**7(1)**	**9(2)**	11(3)	13(4)	15(5)	17(6)	**19(7)**	**21(8)**	23(9)	25(10)	27**(11)**	29(12)	31(13)	33(14)
4n-12	2n+6	8(1)	**10(2)**	12(3)	14(4)	16(5)	18(6)	20**(7)**	**22**(8)	**24(9)**	26(10)	**28(11)**	30(12)	**32(13)**	34(14)
4n-14	2n+7	9(1)	**11(2)**	13(3)	15(4)	17(5)	19(6)	21**(7)**	23(8)	**25(9)**	**27(10)**	**29(11)**	31(12)	33(13)	35(14)
4n-16	2n+8	10(1)	12(2)	14(3)	16(4)	18(5)	20(6)	22**(7)**	24(8)	26(9)	**28(10)**	**30(11)**	32(12)	34(13)	**36(14)**
4n-18	2n+9	11(1)	**13(2)**	15(3)	17(4)	19(5)	21(6)	23**(7)**	25(8)	27(9)	29(10)	**31(11)**	**33(12)**	35(13)	37(14)
4n-20	2n+10	12(1)	**14(2)**	16(3)	18(4)	20(5)	22(6)	24**(7)**	26(8)	28(9)	**30(10)**	32**(11)**	**34**(12)	**36(13)**	38(14)
4n-22	2n+11	13(1)	15(2)	17(3)	19(4)	21(5)	23(6)	25(7)	27(8)	29(9)	31(10)	33(11)	35(12)	**37(13)**	39(14)
4n-24	2n+12	14(1)	16(2)	18(3)	20(4)	22(5)	24(6)	26(7)	28(8)	30(9)	32(10)	34(11)	36(12)	38(13)	40(14)
4n-26	2n+13	15(1)	17(2)	19(3)	21(4)	23(5)	25(6)	27(7)	29(8)	31(9)	33(10)	35(11)	37(12)	39(13)	41(14)
4n-28	2n+14	16(1)	18(2)	20(3)	22(4)	24(5)	26(6)	28(7)	30(8)	32(9)	34(10)	36(11)	38(12)	**40**(13)	42(14)
4n-30	2n+15	17(1)	19(2)	21(3)	23(4)	25(5)	27(6)	29(7)	31(8)	33(9)	35(10)	37(11)	39(12)	**41**(13)	43(14)
4n-32	2n+16	18(1)	20(2)	22(3)	24(4)	26(5)	28(6)	30(7)	32(8)	34(9)	36(10)	38(11)	40(12)	42(13)	44(14)
4n-34	2n+17	19(1)	21(2)	23(3)	25(4)	27(5)	29(6)	31(7)	33(8)	35(9)	37(10)	39(11)	41(12)	43(13)	45(14)

Table 4. A selected portion of K(n) map converted into cluster valence electrons

	Nx	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
4n+8	C^{-3}	**22**	**36**	**50**	**64**	**78**	**92**	106	**120**	134	148	162	176	190	204	218
4n+6	C^{-2}	**20**	**34**	**48**	**62**	**76**	**90**	104	118	**132**	146	**160**	174	188	202	216
4n+4	C^{-1}	**18**	**32**	**46**	**60**	**74**	**88**	102	**116**	**130**	**144**	158	172	186	200	214
4n+2	C^{0}	**16**	**30**	**44**	**58**	**72**	**86**	**100**	**114**	**128**	**142**	**156**	**170**	**184**	**198**	**212**
		[M1]	[M2]	[M3]	[M4]	[M5]	[M6]	[M7]	[M8]	[M9]	[M10]	[M11]	[M12]			
4n+0	C^{1}	**14**	**28**	**42**	**56**	**70**	**84**	**98**	112	126	140	**154**	**168**	**182**	**196**	**210**
4n-2	C^{2}	**12**	26	**40**	**54**	**68**	82	96	**110**	124	138	152	166	180	194	208
4n-4	C^{3}	**10**	**24**	38	**52**	**66**	**80**	94	**108**	**122**	**136**	150	**164**	**178**	**192**	**206**
4n-6	C^{4}	**8**	22	36	50	**64**	**78**	92	106	120	**134**	**148**	**162**	**176**	**190**	**204**
4n-8	C^{5}	**6**	**20**	34	48	62	**76**	**90**	**104**	118	132	**146**	**160**	**174**	**188**	**202**
4n-10	C^{6}	**4**	**18**	32	46	60	74	**88**	**102**	116	130	144	158	172	186	200
4n-12	C^{7}	2	**16**	30	44	58	72	86	**100**	**114**	128	**142**	156	170	184	198
4n-14	C^{8}	0	**14**	28	42	56	70	84	98	**112**	**126**	**140**	154	168	182	196
4n-16	C^{9}	-2	**12**	26	40	54	68	82	96	**110**	**124**	**138**	152	166	180	194
4n-18	C^{10}	-4	**10**	24	38	52	66	80	94	**108**	**122**	**136**	150	164	178	192

Table 5A. Capping series of selected portion of the K(n) map

	[M-1]		[M0]		[M1]		[M2]		[M3]		[M4]		[M5]		[M6]
C^{2}	12	C^{1}	14	C^{0}	16	C^{-1}	18	C^{-2}	20	C^{-3}	22	C^{-4}	24	C^{-5}	26
C^{3}	24	C^{2}	26	C^{1}	28	C^{0}	30	C^{-1}	32	C^{-2}	34	C^{-3}	36	C^{-4}	38
C^{4}	36	C^{3}	38	C^{2}	40	C^{1}	42	C^{0}	44	C^{-1}	46	C^{-2}	48	C^{-3}	50
C^{5}	48	C^{4}	50	C^{3}	52	C^{2}	54	C^{1}	56	C^{0}	58	C^{-1}	60	C^{-2}	62
C^{6}	60	C^{5}	62	C^{4}	64	C^{3}	66	C^{2}	68	C^{1}	70	C^{0}	72	C^{-1}	74
C^{7}	72	C^{6}	74	C^{5}	76	C^{4}	78	C^{3}	80	C^{2}	82	C^{1}	84	C^{0}	86
C^{8}	84	C^{7}	86	C^{6}	88	C^{5}	90	C^{4}	92	C^{3}	94	C^{2}	96	C^{1}	98
C^{9}	96	C^{8}	98	C^{7}	100	C^{6}	102	C^{5}	104	C^{4}	106	C^{3}	108	C^{2}	110
C^{10}	108	C^{9}	110	C^{8}	112	C^{7}	114	C^{6}	116	C^{5}	118	C^{4}	120	C^{3}	122
C^{11}	120	C^{10}	122	C^{9}	124	C^{8}	126	C^{7}	128	C^{6}	130	C^{5}	132	C^{4}	134
C^{12}	132	C^{11}	134	C^{10}	136	C^{9}	138	C^{8}	140	C^{7}	142	C^{6}	144	C^{5}	146
C^{13}	144	C^{12}	146	C^{11}	148	C^{10}	150	C^{9}	152	C^{8}	154	C^{7}	156	C^{6}	158
C^{14}	156	C^{13}	158	C^{12}	160	C^{11}	162	C^{10}	164	C^{9}	156	C^{8}	158	C^{7}	160

Table 5 B. An example to illustrate the values of Tables 4 and 5A

S=4n+q	CVE[M1]	C^y			Fragment		Kp =C^yC[Mx]	Ve =14+2x+12(n-1)
4n-2	12	C^2			AuL^{+1}		C^2C[M-1]	14+2(-1)+12(1-1)=12
4n+2	16	C^0			AuL_2^-		C^0C[M1]	14+2(1)+12(1-1)=16
			-(4n-2)	$-AuL^{+1}$	+(4n-2)	$+AuL^{+1}$		
4n+0	28	C^1			Au_2L_3		C^1C[M1]	14+2(1)+12(2-1) =28
			-(4n-2)	$-AuL^{+1}$	+(4n-2)	$+AuL^{+1}$		
4n-2	40	C^2			$Au_3L_3^-$		C^2C[M1]	14+2(1)+12(3-1) =40
			-(4n-2)	$-AuL^{+1}$	+(4n-2)	$+AuL^{+1}$		
4n-4	52	C^3			Au_4L_4		C^3C[M1]	14+2(1)+12(4-1)=52
			-(4n-2)	$-AuL^{+1}$	+(4n-2)	$+AuL^{+1}$		
4n-6	64	C^4			$Au_5L_4^-$		C^4C[M1]	14+2(1)+12(5-1) =64
			-(4n-2)	$-AuL^{+1}$	+(4n-2)	$+AuL^{+1}$		
4n-8	76	C^5			Au_6L_5		C^5C[M1]	14+2(1)+12(6-1)=76
			-(4n-2)	$-AuL^{+1}$	+(4n-2)	$+AuL^{+1}$		
4n-10	88	C^6			$Au_7L_6^{+1}$		C^6C[M1]	14+2(1)+12(7-1)=88
			-(4n-2)	$-AuL^{+1}$	+(4n-2)	$+AuL^{+1}$		
4n-12	100	C^7			$Au_8L_7^{2+}$		C^7C[M1]	14+2(1)+12(8-1)=100
			-(4n-2)	$-AuL^{+1}$	+(4n-2)	$+AuL^{+1}$		
4n-14	112	C^8			$Au_9L_8^{3+}$		C^8C[M1]	14+2(1)+12(9-1)=112

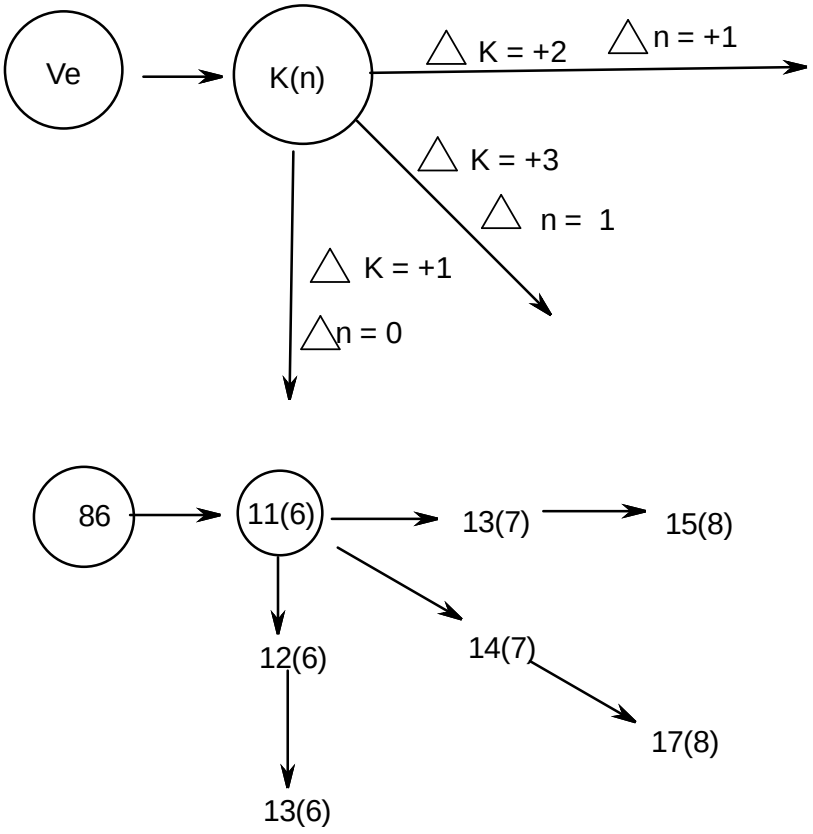
In order to clarify further, the meaning of Tables 4 and 5A, another Table 5B has been included with a specific example. Starting with $Au_9L_8^{3+}$ and removing the capping fragment, AuL^+(Ve = 12), stepwise, we can hypothetically derive the clusters, $Au_8L_7^{2+}$, $Au_7L_6^{+1}$, $Au_7L_6^{+1}$, Au_6L_5, $Au_5L_4^-$, Au_4L_4, $Au_3L_3^-$, Au_2L_3, and AuL_2^- . In principle, all these clusters do possess a single skeletal element in the nucleus while the rest are capping around it. Some of the clusters such as $Au_9L_8^{3+}$, $Au_8L_7^{2+}$, $Au_7L_7^{+1}$, Au_4L_4, AuL_2^- and AuL^{+1} are well known(Mingos,1984; Kiremire,2017e). When changes in Table 5B are closely examined, it is found that they obey the simple algebra of cluster series.

Table 6. The cluster valence electrons for the main group elements corresponding to Table 4

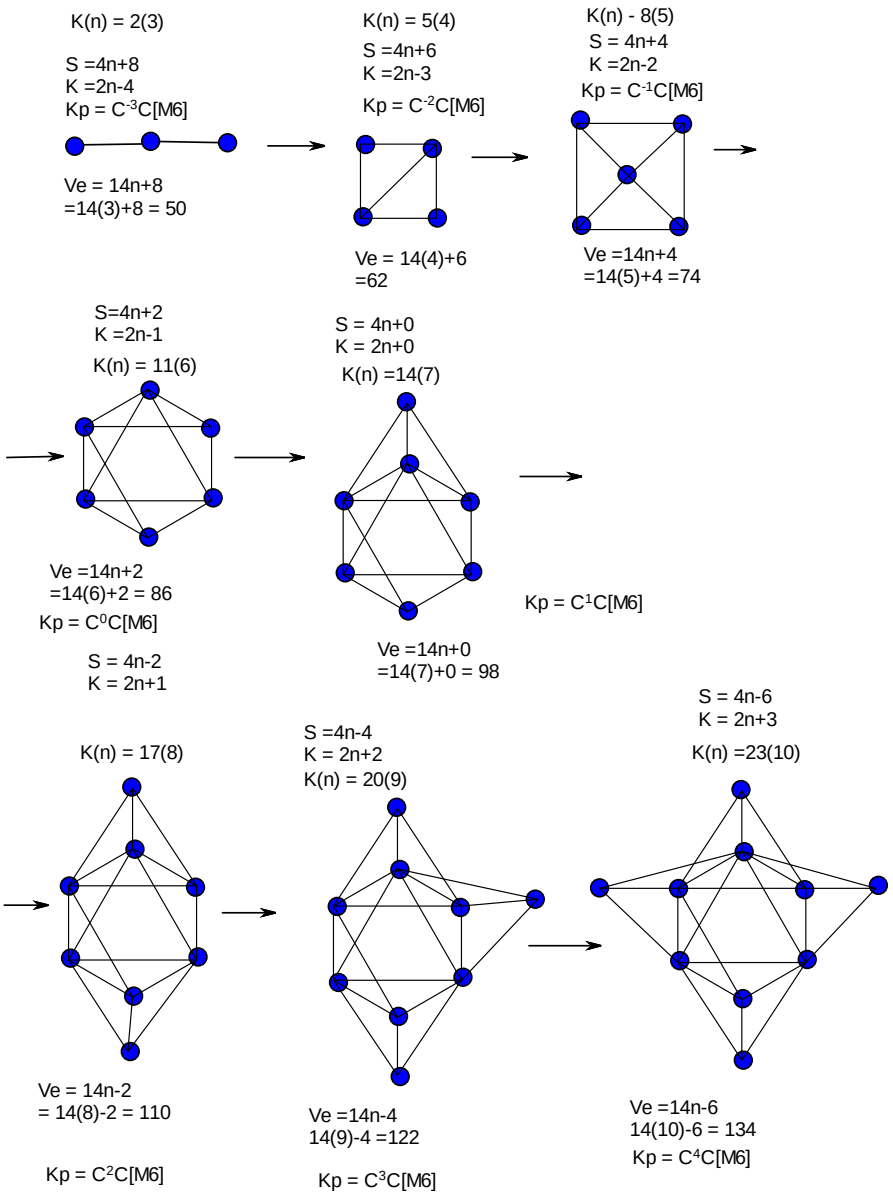
	Nx	1	2	3	4	5	6	7	**8**	9	10	11	12	13	14	15
4n+16		20	24	28	30	36	40	44	**48**	52	56	60	64	68	72	76
4n+14		18	22	26	28	34	38	42	**46**	50	54	58	62	66	70	74
4n+12	C^{-5}	16	20	24	26	32	36	40	**44**	48	52	56	60	64	68	72
4n+10	C^{-4}	14	18	22	24	30	34	38	**42**	46	50	54	58	62	66	70
4n+8	C^{-3}	12	16	20	24	28	32	36	**40**	44	**48**	52	56	60	64	68
4n+6	**C^{-2}**	**10**	**14**	**18**	**22**	**26**	**30**	**34**	38	**42**	**46**	**50**	**54**	**58**	**62**	**66**
4n+4	**C^{-1}**	**8**	**12**	**16**	**20**	**24**	**28**	**32**	**36**	**40**	**44**	**48**	**52**	**56**	**60**	**64**
4n+2	**C^0**	**6**	**10**	**14**	**18**	**22**	**26**	**30**	**34**	**38**	**42**	**46**	**50**	**54**	**58**	**62**
		[M1]	[M2]	[M3]	[M4]	[M5]	[M6]	[M7]	[M8]	[M9]	[M10]	[M11]	[M12]	[M13]	[M14]	[M15]
4n+0	C^1	4	8	12	16	20	24	28	32	36	40	44	48	52	56	60
4n-2	C^2	2	6	10	14	18	22	26	**30**	34	38	42	46	50	54	58
4n-4	C^3	0	4	8	12	16	20	24	28	32	36	40	44	48	52	56

Table 7. Cluster valence electrons of selected main group clusters

CLUSTER	K(n)	SERIES S =4n+q	K(n) SERIES K =2n- ½ q	Kp =$C^{y}C[Mx]$	Ve= 8n-2K
B_2H_6	2(2)	4n+4	2n-2	$C^{1}C[M3]$	12
$B_2H_7^-$	1(2)	4n+6	2n-3	$C^{-2}C[M4]$	14
$B_3H_8^-$	3(3)	4n+6	2n-3	$C^{-2}C[M5]$	18
B_5H_9	8(5)	4n+4	2n-2	$C^{1}C[M6]$	24
B_4H_{10}	5(4)	4n+6	2n-3	$C^{2}C[M6]$	22
B_5H_{11}	7(5)	4n+6	2n-3	$C^{2}C[M7]$	26
$B_5H_{10}^-$	7(5)	4n+6	2n-3	$C^{2}C[M7]$	26
B_6H_{10}	10(6)	4n+4	2n-2	$C^{1}C[M7]$	28
B_6H_{12}	9(6)	4n+6	2n-3	$C^{-2}C[M8]$	30
B_8H_{12}	14(8)	4n+4	2n-2	$C^{1}C[M9]$	36
B_8H_{14}	13(8)	4n+6	2n-3	$C^{-2}C[M10]$	38
B_9H_{15}	15(9)	4n+6	2n-3	$C^{-2}C[M11]$	42
$B_{10}H_{14}$	18(10)	4n+4	2n-2	$C^{1}C[M11]$	44
$B_{10}H_{15}^-$	17(10)	4n+6	2n-3	$C^{-2}C[M12]$	46
$B_{11}H_{13}^{2-}$	20(11)	4n+4	2n-2	$C^{-1}C[M12]$	48
B_8H_{16}	12(8)	4n+8	2n-4	$C^{-3}C[M11]$	40
$B_9H_{14}^-$	15(9)	4n+6	2n-3	$C^{-2}C[M11]$	42
$B_{10}H_{18}$	16(10)	4n+8	2n-4	$C^{-3}C[M13]$	48
$B_1H_1^{2-}$	1(1)	4n+2	2n-1	$C^{0}C[M1]$	6
$B_2H_2^{2-}$	3(2)	4n+2	2n-1	$C^{0}C[M2]$	10
$B_3H_3^{2-}$	5(3)	4n+2	2n-1	$C^{0}C[M3]$	14
$B_4H_4^{2-}$	7(4)	4n+2	2n-1	$C^{0}C[M4]$	18
$B_5H_5^{2-}$	9(5)	4n+2	2n-1	$C^{0}C[M5]$	22
$B_6H_6^{2-}$	11(6)	4n+2	2n-1	$C^{0}C[M6]$	26
$B_7H_7^{2-}$	13(7)	4n+2	2n-1	$C^{0}C[M7]$	30
$B_8H_8^{2-}$	15(8)	4n+2	2n-1	$C^{0}C[M8]$	34
$B_9H_9^{2-}$	17(9)	4n+2	2n-1	$C^{0}C[M9]$	38
$B_{10}H_{10}^{2-}$	19(10)	4n+2	2n-1	$C^{0}C[M10]$	42
$B_{11}H_{11}^{2-}$	21(11)	4n+2	2n-1	$C^{0}C[M11]$	46
$B_{12}H_{12}^{2-}$	23(12)	4n+2	2n-1	$C^{0}C[M12]$	50
$B_{13}H_{13}^{2-}$	25(13)	4n+2	2n-1	$C^{0}C[M13]$	54
$B_{14}H_{14}^{2-}$	27(14)	4n+2	2n-1	$C^{0}C[M14]$	58
$B_{15}H_{15}^{2-}$	29(16)	4n+2	2n-1	$C^{0}C[M15]$	62
CO	3(2)	4n+2	2n-1	$C^{0}C[M2]$	10
N_2	3(2)	4n+2	2n-1	$C^{0}C[M2]$	10
C_2H_2	3(2)	4n+2	2n-1	$C^{0}C[M2]$	10
C_2H_4	2(2)	4n+4	2n-2	$C^{-1}C[M3]$	12
O_2	2(2)	4n+4	2n-2	$C^{-1}C[M3]$	12
F_2	1(2)	4n+6	2n-3	$C^{-2}C[M4]$	14
C_2H_6	1(2)	4n+6	2n-3	$C^{-2}C[M4]$	14
P_4	6(4)	4n+4	2n-2	$C^{-1}C[M5]$	20
C_4H_6	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	22
C_6H_6	9(6)	4n+6	2n-3	$C^{-2}C[M8]$	30
S_8	8(8)	4n+16	2n-8	$C^{-7}C[M15]$	48
S_8^{2+}	9(8)	4n+14	2n-7	$C^{-6}C[M14]$	46



Scheme 2. Relationship within K(n) parameters



Scheme 3. Illustrating the capping process of [M6] clan of clusters

2.3 Derivation of Cluster Valence Electrons From Series Formulas

2.3.1 The K = 2n= ½ q

The cluster valence electrons can be obtained by a simple calculation using one of the series formulas. One of these formulas is Ve = 14n+q for transition metal or Ve = 4n+q for main group elements. A few examples have been included in Scheme 1.

Alternatively, we can use the cluster valence electrons by using a formula that does not include the q determinant. The formula can be derived as follows.

Ve = 14n+q

K =2n- ½ q

Hence ½ q = 2n-K

q = 2[2n-K]

Substituting the value of q in the series formula, we get, Ve = 14n+q = 14n+q = 14n+4n-2K = 18n-2K.

For the main group element, Ve = 4n+q = 4n+4n-2K = 8n-2K.

Therefore we use, Ve = 18n-2K for transition metal clusters and Ve = 8n-2K for the main group element clusters.

2.3.2 The Equivalence Relationship

Ve = S = 14n+q =18n-2K (Transition metals) or Ve = 4n+q =8n-2K (Main group elements).

Examples

Ex-1: K(n) = 3(3); n =3, K = 3, S = 4n+6, Ve = 14n+6 = 14(3)+6 = 48 or Ve = 18n-2K =18(3)-2(3) = 48, Ve =4n+6 = 4(3)+6 =18 or Ve =8n-2K= 8(3)-2(3) = 18.

Similar calculations can be done for main group element clusters. The following examples focus on transition metal clusters and main group element clusters using one type of the cluster valence formulas.

Ex-2: K(n) = 6(4); n = 4, K = 6, Ve = 18(4)-2(6) = 60, Ve = 8(4)-2(6) = 20

Ex-3: K(n) = 9(5); n=5,K=9, Ve = 18(5)-2(9) = 72, Ve = 8(5)-2(9) =22

Ex-4: K(n) = 11(6); n = 6, K = 11, Ve = 18(6)-2(11) = 86, Ve = 8(6)-2(11) = 26

Ex-5: K(n) = 12(6); n = 6, K = 12, Ve = 18(6)-2(12) = 84, Ve = 8(6)-2(12) = 24

Ex-6: K(n)= 8(5); n =5, K=8, Ve = 18(5)-2(8) = 74, Ve = 8(5)-2(8) = 24

Ex-7:K(n) = 14(7); n =7, K= 14, Ve=18(7)-2(14) = 98, Ve = 8(7)-2(14) = 28

Ex-8: K(n) = 17(8); n =8, K = 17, Ve = 18(8)-2(17) = 110,Ve =8(8)-2(17) = 30

Ex-9: K(n) = 20(9); n = 9, K = 20, Ve = 18(9)-2(20) = 122, Ve = 8(9)-2(20) = 32

Ex-10: K(n) = 23(10); n=10, K = 23, Ve = 18(10)-2(23) = 134, Ve = 8(10)-2(23) = 34.

In earlier work (Kiremire, 2015a-c), the cluster parameter K(n) was calculated by using the empirically derived formula K = ½ [E-V], where E represented the total 18 valence electrons of the skeletal elements of transition metal atoms and V = the total number of the valence electrons of the skeletal elements and the ligands. In the case of the main group elements, E represented the sum of 8 electron valence electrons of the skeletal elements and V the sum of the valence electrons of the skeletal elements and the ligands. The above derivation of the cluster valence electrons, Ve = 18n-2K- clearly shows the similarity of the relationships. Let us reflect on the meaning of K(n) parameter further by looking at a few more simple examples. Take the dinitrogen molecule, N_2: K =2[1.5] =3; K(n) =3(2), Ve =8n-2K =8(2)-2(3) =10; C_2H_2: K =2[2]-2(0.5) =3, K(n) =3(2), Ve =8n-2K =8(2)-2(3) =10; C_2H_4: K =2[2]-4(0.5) =2, K(n) =2(2), Ve =8n-2K =8(2)-2(2) =12; O_2: K =2[1] = 2, K(n) =2(2), Ve =8n-2K =8(2)-2(2) =12; F_2: K =2[0.5] = 1, K(n) =1(2), Ve =8n-2K =8(2)-2(1) =14;$Mn_2(CO)_{10}$: K =2[5.5]-10(1) = 1, K(n) =1(2), Ve =18n-2K =18(2)-2(1) =34; $Rh_2(Cp)_2(CO)_2$:K =2[4.5]-2(2.5)-2(1) =2, K(n) = 2(2), Ve =18n-2K =18(2)-2(2) =32; $Rh_2(Cp)_2(CO)_2$:K =2[4.5]-2(2.5)-2(1) =2, K(n) = 2(2), Ve =18n-2K =18(2)-2(2) =32; $Mo_2(Cp)_2(CO)_4$, K =2[6]-2(2.5)-4(1) =3, K(n) = 3(2), Ve =18n-2K =18(2)-2(3) =30; $B_6H_6^{2-}$:K = 6[2.5]-6(0.5)-2(0.5) = 11; K(n) = 11(6), Ve= 8n-2K =8(6)-2(11) = 26; $Rh_6(CO)_{16}$:K = 6[4.5]-16(1) = 11; K(n)=11(6);Ve=18n-2K = 18(6)-2(11) = 86; $Os_6(CO)_{16}^{2-}$:K = 6[4.5]-16(1) = 11; K(n)=11(6);Ve=18n-2K = 18(6)-2(11) = 86; $Os_7(CO)_{21}$:K = 7[5]-21(1) = 14; K(n)=14(7);Ve=18n-2K = 18(7)-2(14) =98; $Os_8(CO)_{22}^{2-}$:K = 8[5]-22(1)-2(0.5) = 17; K(n)=17(8);Ve=18n-2K = 18(8)-2(17) =110. From these few illustrative examples, it makes a lot of sense if we regard K as having the same meaning as 'chemical bond(s)'. Thus, K(n) = 3(2), means 3 chemical bonds that link up 2 skeletal elements as in N_2, 2(2)-meaning 2 chemical bonds linking up 2 skeletal elements as in C_2H_4; 9(5)-meaning 9 skeletal bonds linking up 5 skeletal elements as in $Sn_5^{2-}$and 11(6)- as eleven skeletal bonds linking up 6 skeletal elements as in $B_6H_6^{2-}$and so on. The simple calculation Ve =8n-2K(main group elements) or Ve = 18n-2K (transition metals) predicts or assigns the exact number of cluster valence electrons that the cluster will have. Hence the K(n) parameter embodies the number of bonds and its corresponding skeletal elements that cluster possesses or it can be regarded as the number of electron pairs that cluster requires for each of its skeletal elements to achieve a noble gas electron configuration. This underpins the great significance of the K(n) map which gives an array of chemical bonds and their corresponding skeletal elements as well as their corresponding inherent cluster valence electron contents.

2.3.3 The K = ½ [E-V] Formula

The above formula was empirically derived in earlier work (Kiremire, 2015a, 2015d). If we examine the relationship Ve = 18n-2K, then 2K = 18n-Ve, and hence K = ½ [18n-Ve] = ½ [E-V], where E = 18n, V = Ve. The same procedure can be done for the main group elements. Applying the formula, Ve = 18n-2K, the cluster valence electrons that correspond to commonly encountered K(n) values have been calculated and are given in Table 8

2.4 Characteristic Cluster Valence Electron Counts and Geometrical Shapes

From the studies of series and their skeletal numbers, it is very clear that the cluster valence electrons are a consequence of the K(n) parameters. This is demonstrated in Table 8. The characteristic numbers have been used as a guide to predict

the skeletal shapes of clusters (Housecroft & Sharpe, 2005; Fehlner & Halet, 2007).

Table 8. The origin of characteristic cluster valence electrons usually cited for Transition Metals

CLUSTER NAME	NUCLEARITY INDEX, Mx	POSSIBLE K(n)	S=4n+q	K =2n-(1/2)q	Ve = 14n+q	Ve =18n-2K
Monomer	M1	0(1)	4n+4	2n-2	14(1)+4 =18	18(1)-0 =18
Dimer	M2	1(2)	4n+6	2n-3	14(2)+6 = 34	18(2)-2(1) =34
Linear or bent	M3	2(3)	4n+8	2n-4	14(3)+8 = 50	18(3)-2(2)=50
Trimer	M3	3(3)	4n+6	2n-3	14(3)+6 =48	18(3)-2(3)=48
Tetrahedron	M4	6(4)	4n+4	2n-2	14(4)+4 = 60	18(4)-2(6)=60
Butterfly	M4	5(4)	4n+6	2n-3	14(4)+6 =62	18(4)-2(5)=62
Square	M4	4(4)	4n+8	2n-4	14(4)+8 =64	18(4)-2(4)=64
Trigonal bypyramid	M5	9(5)	4n+2	2n-1	14(5)+2 = 72	18(5)-2(9)=72
Square pyramid	M5	8(5)	4n+4	2n-2	14(5)+4 =74	18(5)-2(8)=74
Bicapped tetrahedron	M6	12(6)	4n+0	2n+0	14(6)+0 = 84	18(6)-2(12)=84
Octahedron	M6	11(6)	4n+2	2n-1	14(6)+2 =86	18(6)-2(11)=86
Pentagonal pyramid	M6	10(6)	4n+4	2n-2	14(6)+4 =88	18(6)-2(10)=88
Trigonal prism	M6	9(6)	4n+6	2n-3	14(6)+6 =90	18(6)-2(9)=90
Monocapped octahedron	M7	14(7)	4n+0	2n+0	14(7)+0 = 98	18(7)-2(14)=98
Bicapped octahedron	M8	17(8)	4n-2	2n+1	14(8)-2 = 110	18(8)-2(17)=110
Triangular dodecahedron	M8	16(8)	4n+0	2n+0	14(8)+0 =112	18(8)-2(16)=112
Square antiprism	M8	15(8)	4n+2	2n-1	14(8)+2 = 114	18(8)-2(15)=114
Cube	M8	12(8)	4n+8	2n-4	14(8)+8=120	18(8)-2(12)=120
Tetracapped octahedron	M10	23(10)	4n-6	2n+3	14(10)-6 =134	18(10)-2(23)=134
Truncated hexagonal bipyramid	M12	23(12)	4n+2	2n-1	14(12)+2 =170	18(12)-2(23)=170
Icosahedron	M12	23(12)	4n+2	2n-1	14(12)+2 =170	18(12)-2(12)=170
Cube octahedron	M12	23(12)	4n+2	2n-1	14(12)+2 =170	18(12)-2(12)=170

2.5 The Geometrical Puzzles of Some Clusters and the Series Approach

2.5.1 Geometries of Certain Clusters Are Usually Associated With Specific Cluster Valence Electron Contents

For instance, in case of transition metal clusters, (i) a triangular skeletal shape is associated with a cluster valence content of 48. If this information is carefully analyzed, it implies that there are three (3) skeletal linkages to three (3) skeletal elements and therefore we can express this as K(n) = 3(3). Arising from this, K = 2n-q/2 =3= 2(3) –q/2; q =6; and S = 4n+6. This formula is good for the categorization of all the clusters which belong to the arachno family. Since we are dealing with the transition metals, the equation is adjusted to S=14n+6 for the sole purpose of calculating cluster valence electron contents. Hence, the valence electron content is easily be calculated using the formula Ve = 14n+6. Since n = 3, Ve = 14(4)+6 = 48. It is clear that the K(n) parameter dictates the cluster valence electron content. This means any cluster of K(n) = 3(3) parameter will fit into the slot of valence electron content of 48. As discussed earlier, once we know the K(n) parameter of a cluster, we can directly apply the formula Ve = 18n-2K to calculate the cluster valence electron content without deriving the series formula. Thus, Ve = 18n-2k = 18(3)-2(3) = 48.

(ii) Another good example is a tetrahedral cluster which is associated with an electron count of 60. In this example, a tetrahedral geometry has 6 linkages binding 4 skeletal elements, so K(n) = 6(4); Ve = 18n-2K = 18(4)-2(6) = 60.

(iii) A butterfly of planar raft, K(n) = 5(4); Ve = 18n-2K = 18(4)-2(5) = 62.

(iv) A square, K(n) = 4(4); Ve = 18n-2K = 18(4)-2(4) = 64.

(v) A trigonal bipyramid; K(n) = 9(5), Ve = 18(5)-2(9) = 72.

(vi) A square pyramid; K(n) = 8(5), Ve = 18n-2K = 18(5)-2(8) = 74 and a

(vii) Trigonal prism; K(n) =9(6), Ve = 18n-2K = 18(6)-2(9) = 90.

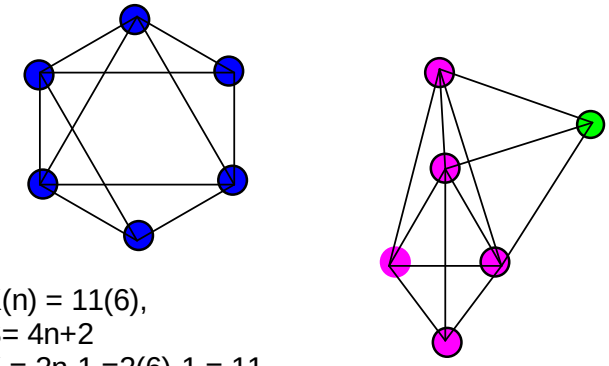
Clearly, the K(n) parameter, dictates the cluster valence electron content of the respective cluster.

2.5.2 Cluster Puzzles

(a) The puzzle arises as to why $Os_6(CO)_{18}^{2-}$ adopts an octahedral shape whereas $Os_6(CO)_{18}$ does not (Housecroft&Sharpe,2005). According to the series approach, these two clusters have different K(n) parameters. The K value of $Os_6(CO)_{18}^{2-}$ is given by K = 6[5]-18-1 = 11; K(n) = 11(6), S = 4n+2, and therefore, it is a member of the CLOSO family which normally adopts an octahedral shape, O_h. The cluster $Rh_6(CO)_{16}$; K = 6[4.5]-16 = 11, K(n) = 11(6), S = 4n+2, also belongs to a CLOSO family associated with the ideal octahedral

skeletal geometry, O_h. The expected cluster valence electron content, Ve = 18n-2K = 18(6)-2(11) = 86. Thus, the ideal octahedral cluster shape for transition metal cluster is usually characterized by a valence electron content of 86.

The K value of $Os_6(CO)_{18}$ is given by K = 6[5]-18 = 12; K(n) = 12(6), S = 4n+0, this means the cluster is a member of mono-capped series. This implies that one of the skeletal elements is capping on the remaining ones and the symbol for this is, $Kp = C^1C[M5]$. This symbol predicts that the ideal shape will be a trigonal bipyramid with one capping skeletal element. The ideal shapes of the two types of clusters are shown in Figure 7.



K(n) = 11(6),
S= 4n+2
K = 2n-1 =2(6)-1 = 11
Ve =14n+2 = 14(6)+2 = 86

$Kp = C^0C[M6]$

This is an ordinary octahedral cluster.

K(n) = 12(6),
S= 4n+0
K = 2n-1 =2(6)-0 = 12
Ve =14n+) = 14(6)+0 = 84

$Kp = C^1C[M5]$

According to series, this is a mono-capped trigonal bipyramid cluster.

= CAPPING ELEMENT

Figure 7. The sketches of skeletal shapes of ideal octahedral and mono-capped trigonal bipyramid

(b) The clusters with Ve = 76 having a characteristic trigonal bipyramid shape.

i. $Ni_5(CO)_{12}^{2-}$: K = 5[4]-12-1 = 7, K(n) = 7(5), Ve = 18n-2K = 18(5)-2(7) = 76; S = 4n+6, belongs to ARACHNO family.

ii. $Rh_5(CO)_{15}^{-}$: K = 5[4.5]-15-0.5 = 7, K(n) = 7(5), Ve = 18n-2K = 18(5)-2(7) = 76; S = 4n+6, ARACHNO family as well.

iii. $Rh_5(CO)_{14}(I)^{2-}$:4[4.5]-14-0.5-1 = 7, K(n) = 7(5), Ve = 18n-2K = 18(5)-2(7) = 76; S = 4n+6, ARACHNO also.

iv. $Ni_3Mo_2(CO)_{16}^{2-}$: K = 3[4]+2[6]-16-1 = 7, K(n) = 7(5), Ve = 18n-2K = 18(5)-2(7) = 76; S = 4n+6, ARACHNO

v. $RuIr_4(CO)_{15}^{2-}$: K = 1[5]+4[4.5]-15-1 = 7, K(n) = 7(5), Ve = 18n-2K = 18(5)-2(7) = 76; S = 4n+6, ARACHNO

These are described as elongated trigonal bipyramid clusters (Teo, et al, 1984).

(c) i. $Os_5(CO)_{15}^{2-}$: K = 5[5]-15-1 = 9, K(n) = 9(5), Ve = 18n-2K = 18(5)-2(9) = 72, S = 4n+2, CLOSO

ii. $Os5(CO)_{16}$: K = 5[5]-16 = 9, K(n) = 9(5), Ve = 18n-2K = 18(5)-2(9) = 72, S = 4n+2, CLOSO

iii. $PtRh_4(CO)_{12}^{2-}$: 1[4]+4[4.5]-12-1 = 9, K(n) = 9(5), Ve = 18n-2K = 18(5)-2(9) = 72, S = 4n+2, CLOSO

These are described as regular trigonal bipyramid clusters (Teo, et al, 1984).

The ideal shapes of both types of trigonal bipyramid clusters are sketched in Figure 8. Clearly, the two types of clusters are different.

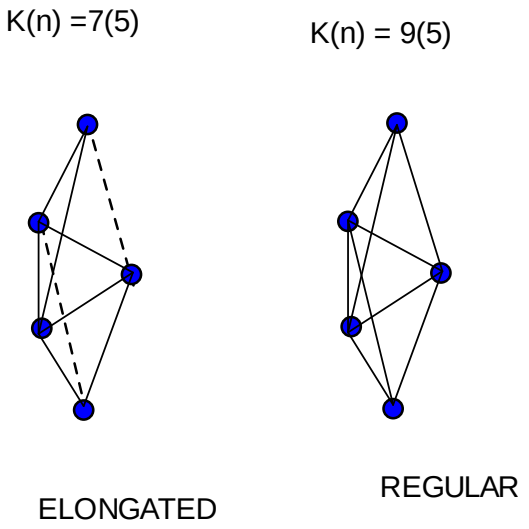
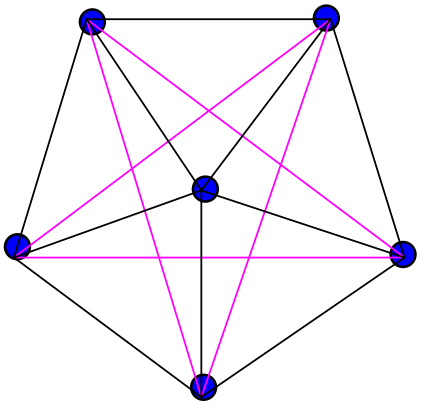


Figure 8. The sketches of ideal elongated and regular trigonal bipyramid

(d) The cluster, $Rh_9(CO)_{19}^{3-}$ is considered to violate the rules of total valence electron counting(Housecroft&Sharpe,2005). The K value of the cluster is given by K =9[4.5]-19-1.5 = 20; K(n) = 20(9), S =4n-4, Kp = C^3C[M6]. Thus, according to series method, the cluster may be regarded as a tri-capped octahedral complex. Its cluster valence electron content is given by Ve = 18n-2K = 18(9)-2(20) = 122. The cluster is expected to have the shape similar to the one predicted for 124 electron count derived from topology (Teo, et al, 1984). By applying the same formula, Ve = 124 = 18(9)-2K, we get the value of K = 19, and therefore, K(n) = 19(9), with the corresponding series formula S =4n-2 and Kp = C^2C[M7]. This implies the 124 electron count belongs to a cluster that could be described as a bi-capped pentagonal bipyramid.

(e) The rhenium cluster $(H)_5Re_6(CO)_{24}^-$ is described as an open cluster rather than an expected closed one(Housecroft &Sharpe, 2005). We can also analyze this cluster using the series method. The K value of the cluster is given by K = 6[5.5]-2.5-24-0.5 = 6, K(n) = 6(6), S = 4n+12. This series formula is similar to that of cyclohexene, C_6H_{12}, K = 6[2]-6= 6, K(n) = 6(6), S = 4n+12. Therefore, the two clusters belong to the same family series and both will be expected to portray similar skeletal geometries as is indeed observed in literature (Housecroft &Sharpe, 2005).

(f) $Rh_6L_6H_{12}^{2+}$: This cluster described as adopting an octahedral shape (Housecroft & Sharpe, 2005) despite having 10 electrons short of the expected valence electron counting. This cluster can also be analyzed by using the series method. The K value of the cluster is given by K =6[4.5]-6-6+1 = 16; K(n) = 16(6), S = 4n-8, K =2n+4, Kp = C^5C[M1]. This means the cluster has a single element in the cluster nucleus which capped by 5 remaining skeletal elements. The are 2 possible skeletal shapes for the cluster. The observed octahedral cluster is a disguised shape of a highly capped cluster similar to those found in golden clusters (Mingos, 1984a; Kiremire, 2017f, 2018a, 2018b). Two possible isomeric skeletal shapes are shown in Figure 9. The observed shape was the octahedral one, Figure 9(B**).** Its cluster valence electron content can readily be calculated using the series valence formula Ve =14n-8 =14(6)-8 = 76 or using its K(n) parameter. Thus, Ve = 18n-2K = 18(6)-2(16) = 76. Since the ordinary octahedral clusters are associated with K(n) =11(6), the rhodium cluster ,$Rh_6L_6H_{12}^{2+}$ with K(n) = 16(6) is an octahedral bound with 5 extra linkages as compared to a regular octahedral clusters. Therefore, it is possible that the rhodium cluster will possess shorter M-M skeletal bonds than the ordinary octahedral skeletal symmetry.



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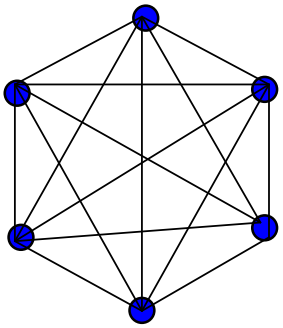


B

Figure 9. Sketches of possible capping skeletal shapes of $Rh_6L_6H_{12}^{2+}$

(g) Some unique rhenium borane clusters (Fehlner& Halet,2007).

Let us examine the series $(ReCp^*)_2(BH)_m$, m =6-10 using the series method.

i. $(ReCp^*)_2(BH)_6$; K =2[5.5-2.5]+6[2.5-0.5] = 2[3]+6[2] = 18, K(n) = 18(8), S = 4n-4, K =2n+2, Kp = C^3C[M5] . This means, the ideal skeletal shape of the cluster will be a tri-capped trigonal bipyramid. The cluster valence electron content can readily be calculated from the adjusted series formula Ve =4n-4 +2(10)= 4(8)-4+20 = 48; VF = 2[7+5]+6[3+1] =48, VF = cluster valence electrons calculated from the cluster formula. The valence electron adjustment comes from the established isolobal type of relationship between main group clusters and transition metal clusters(Kiremire,2018c).

That is, $S = 4n+q \overset{+10n}{\underset{-10n}{\rightleftarrows}} S=14n+q$

ii. $(ReCp^*)_2(BH)_7$; K =2[5.5-2.5]+7[2.5-0.5] = 2[3]+7[2] = 20, K(n) = 20(9), S = 4n-4, K =2n+2, Kp = C^3C[M6]. The predicted ideal skeletal shape is a tri-capped octahedral shape. This is sketched in Figure 11**.**The cluster valence electrons are readily calculated from the series adjusted relationship.

Ve = 4n-4+10(2) = 4(9)-4+20 = 52, VF = 2[7+5]+7[3+1] = 24+28 =52

$ReCp^*)_2(BH)_8$; K =2[5.5-2.5]+8[2.5-0.5] = 2[3]+8[2] = 22, K(n) = 22(10), S = 4n-4, K =2n+2, Kp = C^3C[M7]. The series method predicts an ideal skeletal structure of a tri-capped pentagonal bipyramid. The sketch is shown in Figure 12. The valence electron content is given by Ve =4n-4 +10(2) = 4(10)-4+20 = 56, VF = 2[7+5]+8[3+1]=56.

iii. $ReCp^*)_2(BH)_9$; K =2[5.5-2.5]+9[2.5-0.5] = 2[3]+9[2] = 24, K(n) = 24(11), S = 4n-4, K =2n+2, Kp = C^3C[M8], Ve = 4n-4+10(2)=4(11)-4+20=60, VF= 2[7+5]+9[3+1] = 60. An ideal skeletal sketch is given in Figure 13.

iv. $ReCp^*)_2(BH)_{10}$; K =2[5.5-2.5]+10[2.5-0.5] = 2[3]+10[2] = 26, K(n) = 26(12), S = 4n-4, K =2n+2, Kp = C^3C[M9], Ve = 4n-4+10(2)=4(12)-4+20=64, VF= 2[7+5]+10[3+1] = 64. An ideal skeletal sketch is given in Figure 14.

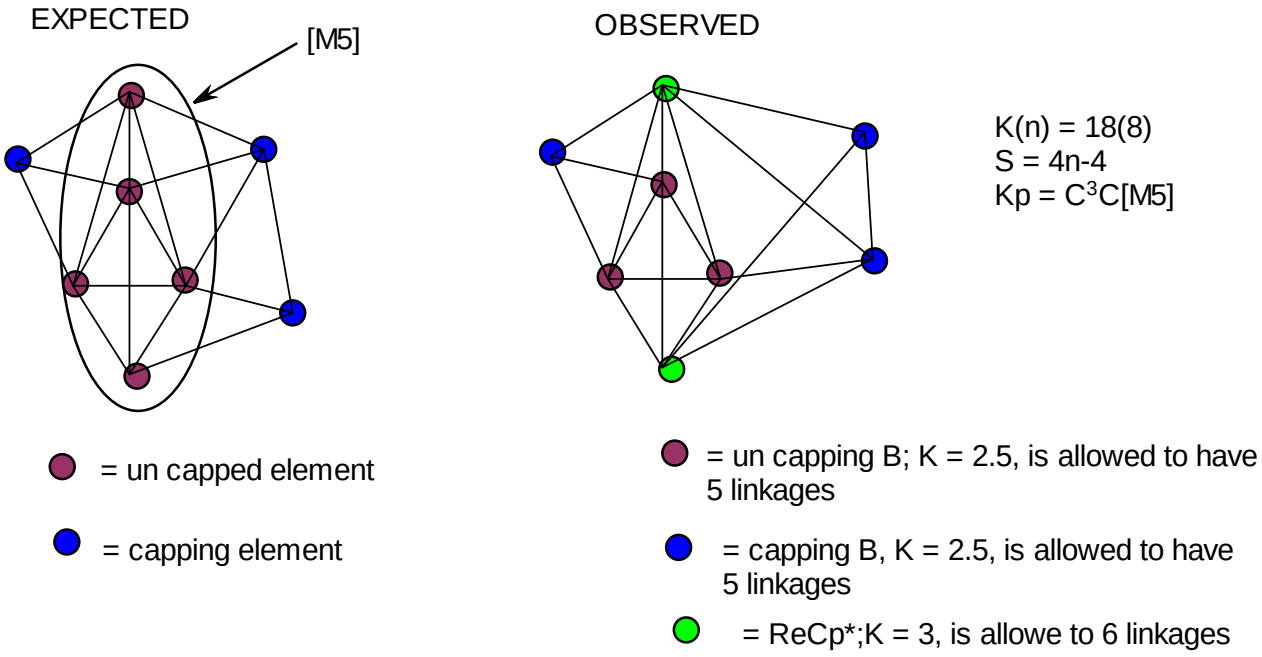


Figure 10. Ideal skeletal sketches of $(ReCp^*)_2(BH)_6$

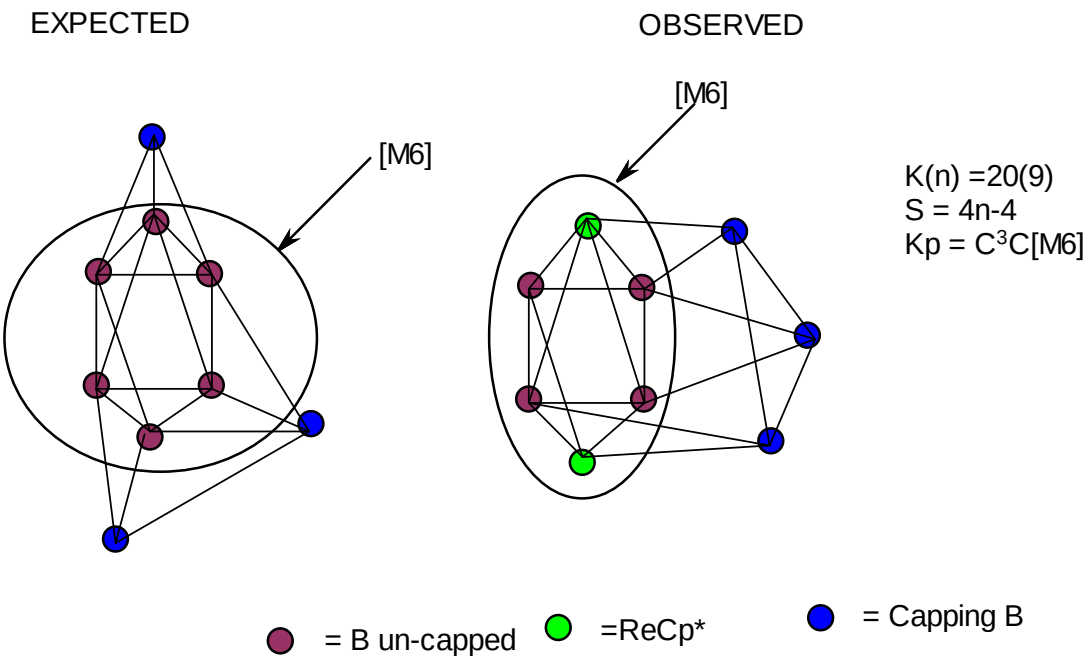
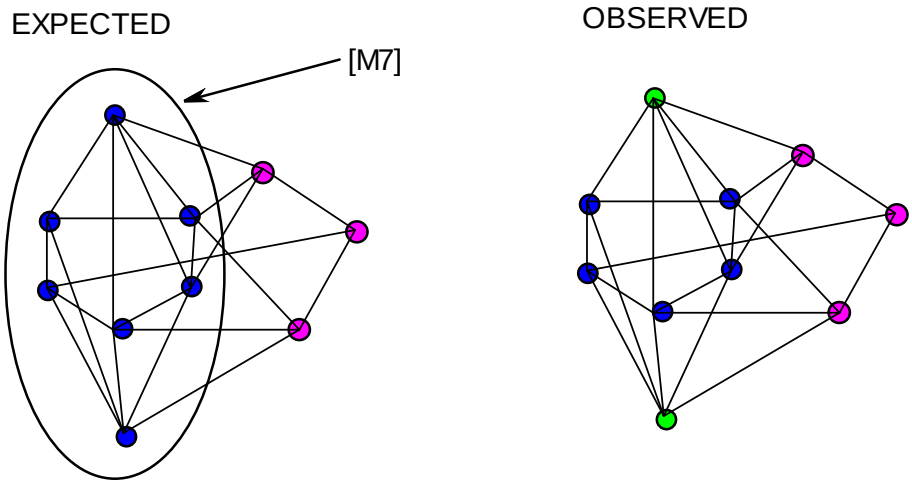


Figure 11. Ideal skeletal sketches of $(ReCp^*)_2(BH)_7$



K(n) = 22(10): S = 4n-4, Kp = C^3C[M7]

Figure 12. Ideal skeletal shape of $(ReCp^*)_2(BH)_8$

$(ReCp^*)_2(BH)_9$:K= 2[5.5-2.5]+9[2.5-0.5] =24, K(n) =24(11), S=4n-4, Kp=C^3C[M8]

The ideal shape is a tri-capped cluster of [M8] closo unit similar to that of $B_8H_8^{2-}$.

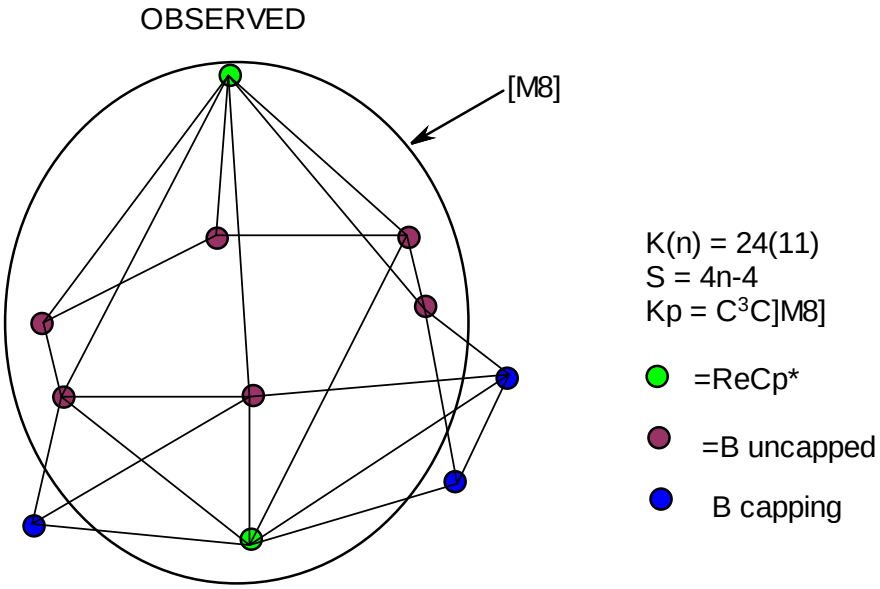


Figure 13. Sketch of Ideal shape of $(ReCp)_2(BH)_9$

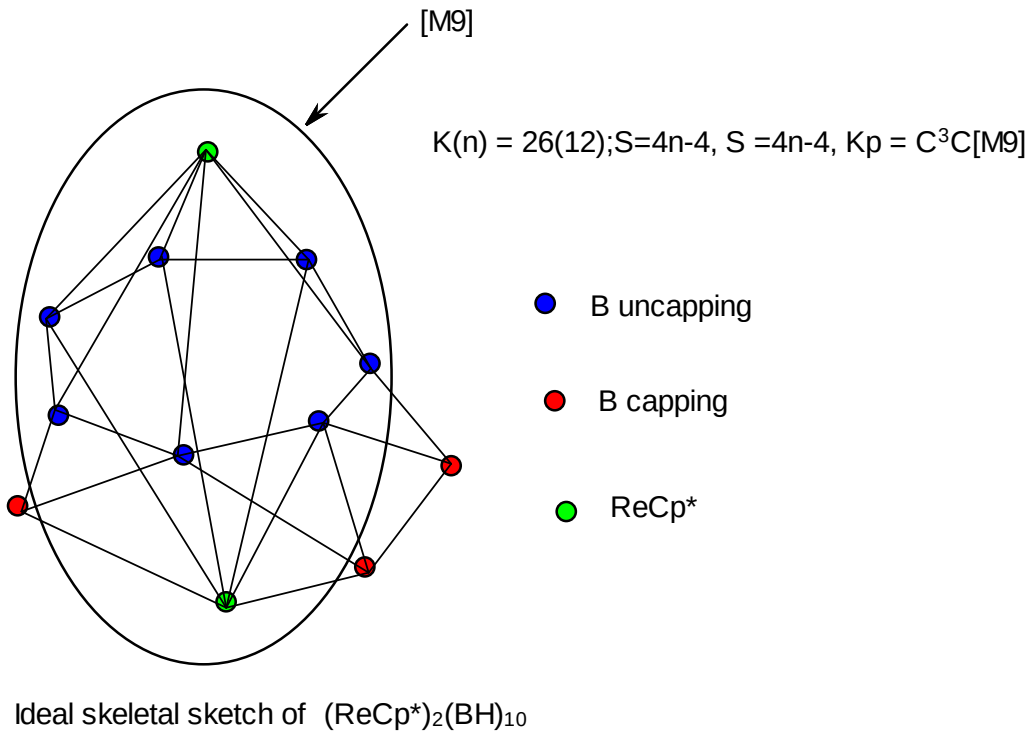


Figure 14. Ideal skeletal sketch of $(ReCp^*)_2(BH)_{10}$

The variations in the clusters, as [BH] fragments are being added are explained in the series Scheme 4A.

n=8	$(ReCp^*)_2(BH)_6$	S =4n-4	Kp = C^3C[M5]	Ve = 4n-2+10(2) =	50
	↓ BH	S =4n+0			
n =9	$(ReCp^*)_2(BH)_7$	S =4n-4	Kp = C^3C[M6]	Ve = 4n-2+10(2) =	54
	↓ BH	S =4n+0			
n =10	$(ReCp^*)_2(BH)_8$	S =4n-4	Kp = C^3C[M7]	Ve = 4n-2+10(2) =	58
	↓ BH	S =4n+0			
n =11	$(ReCp^*)_2(BH)_9$	S =4n-4	Kp = C^3C[M8]	Ve = 4n-2+10(2) =	62
	↓ BH	S =4n+0			
n=12	$(ReCp^*)_2(BH)_{10}$	S =4n-4	Kp = C^3C[M9]	Ve = 4n-2+10(2) =	66

Scheme 4A. Variations of series formula as BH fragment is added

In the above clusters, S = 4n-4 since the added fragment [BH] belongs to the series S = 4n+0.

Thus, S_1 = 4n-4 + S_2 = 4n+0 = (4n-4)+(4n-0) = 4n-4; there is no change in the type of series. Therefore all the

Clusters will be tri-capped, except that the size of the nucleus will vary in size as in this case

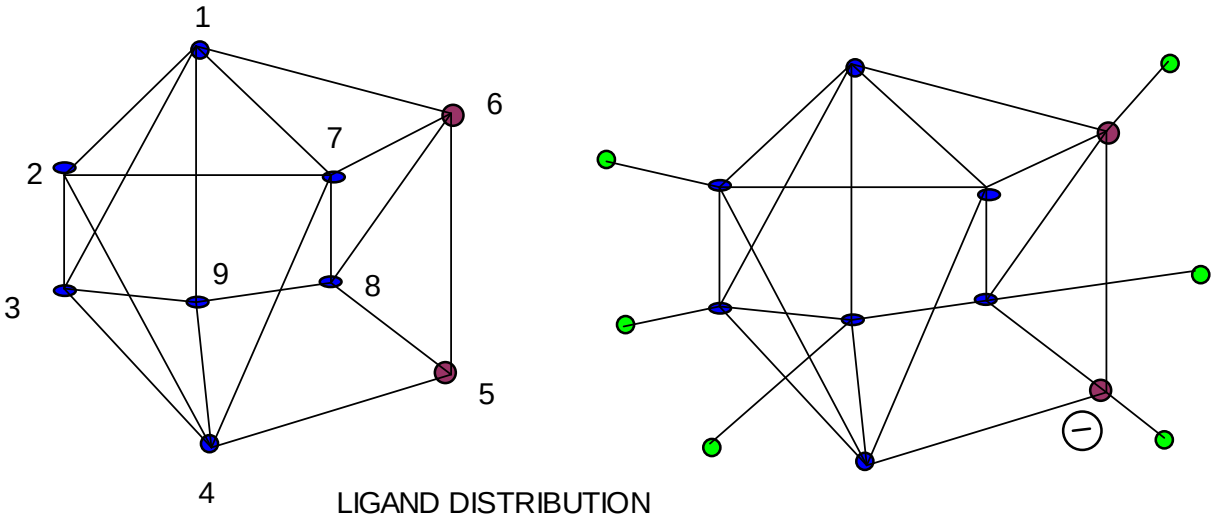
[M5]→[M6]→[M7]→[M8]→[M9]. The fragment [BH], S =4n+0, has a determinant q =0. The concept of determinant was discussed earlier (Kiremire, 2016a, 2016c, 2017c).

(h) A gallium cluster, $Ga_9R_6^{-}$ is also reported to disobey the rule of cluster valence electron counting (Fehlner & Halet, 2007).

This cluster can also be analyzed by using the series method as follows; its K value is given by K = 9[2.5]-3-0.5 = 19; K(n) = 19(9), S = 4n-2, Kp = C^2C[M7]. According to the series method, the cluster is expected to be a bi-capped pentagonal bipyramid. This is sketched in Figure 15. The ligand distribution around gallium skeletal elements shows that 3 skeletal elements will have no ligands attached to them as is the case (Fehlner & Halet, 2007)

$Ga_9R_6^{-}$ K = 9[2.5]-3-0.5 = 19;K(n) =19(9), S = 4n-2, K = 2n+1, Kp = C^2C[M7]

Ve = 4n-2 = 4(9)-2 = 34, or Ve = 8n-2K = 8(9)-2(19)=34; VF =9[3]+6+1 = 34.



LIGAND DISTRIBUTION

k1 = 1[2.5]-5(0.5) = 0
k2 =1[2.5]-4(0.5) = 0.5
k3 =1[2.5]-4(0.5) = 0.5
k4 =1[2.5]-5(0.5)=0
k5= 1[2.5]-3(0.5) = 1
k6 = 1[2.5]-4(0.5)= 0.5
k7= 1[2.5]-5(0.5) = 0
k8 = 1[2.5]-4(0.5)=0.5
k9=1[2.5]-4(0.5) = 0.5

= capping Ga

= uncapping Ga

= R

Figure15. Possible isomeric sketch of $Ga_9R_6^{-}$ with ligand distribution

Calculation of cluster valence electron content of golden clusters

- $Au_{13}Cl_2L_{10}^{3+}$: K = 13[3.5]-1-10+1.5 =36, K(n) =36(13), S = 4n-20, Kp = $C^{11}C$[M2].

The series formula Ve = 14n-20 = 14(13)-20 =162, and the other series formula Ve =18n-2K = 18(13)-2(36) =162.

In addition, the formula, Ve = 14+2x+12(n-1) =18+12(12) = 162{x refers to nuclear index from [Mx] of the cluster, in this case, x = 2} is used to obtain cluster valence electron content of some gold clusters (Fehlner & Saillard, 2007). Since the cluster is a member of [M2] clan, the constant number [18] used in the calculation corresponds to beginning number of [M2] capping series presented in Table 5.

- Another golden cluster $Au_9L_8^{3+}$: K=9[3.5]-8+1.5 =25, K(n) = 25(9), S =4n-14, Kp = C^8C[M1], Ve= 14n-14 =14(9)-14=112; Ve = 18n-2K = 18(9)-2(15)=112; another formula Ve =14+2x(x=1)+12(n-1)= 16+12(8) =112 is applied to calculate the cluster valence electron content (Fehlner & Saillard, 2007). Again the constant [16] corresponds to the number 16 which is same as the one which the beginning of [M1] series which is shown in Table 5.
- Generalization of formulas:

By analyzing the series in Table 5, the two formulas Ve = 18+12n and Ve =16+12n, we can be transformed into a general formula which can be applied to all clusters. This is translated into the form:

Ve = 14+2x +12(n-1);

where Ve = cluster valence electrons, $V_{[Mx]}$ = valence electrons of the nuclear cluster, n= number of skeletal elements of the cluster and the figure 12 refers to the capping constant shown in Table 5B.

Take the above examples as illustrations; $Au_{13}Cl_2L_{10}^{3+}$: Kp = $C^{11}C$[M2], [Mx] = [M2], **Ve** = 14+2x(x=2) +12(n-1**)** = 18+12(12) = 162, VF = 13[11]+2+20-3 =162(from cluster formula).

Another example, $Au_9L_8^{3+}$: Kp = C^8C[M1], [Mx] = [M1], V[Mx]= 16; hence Ve = 14+2x(x=1)+12(n-1) = 16+12(9-1) = 112, VF =9[11]+16-3 = 112. Let us consider a few more examples.

$Au_6L_6^{2+}$:K =6[3.5]-6+1 = 16,K(n) =16(6), S = 4n-8, Kp =C^5C[M1], [Mx] =[M1], Ve = 14+2x(x=1)+12(n-1) = 16+12(6-1) = 76, VF = 6[11]+12-2 = 76.

$Au_7L_7^{+}$: K =7[3.5]-7+0.5 = 18,K(n) =18(7), S = 4n-8, Kp =C^5C[M2], [Mx] =[M2], Ve =14+2x(x=2)+12(n-1) = 18+12(7-1) = 90, VF = 7[11]+14-1 = 90.

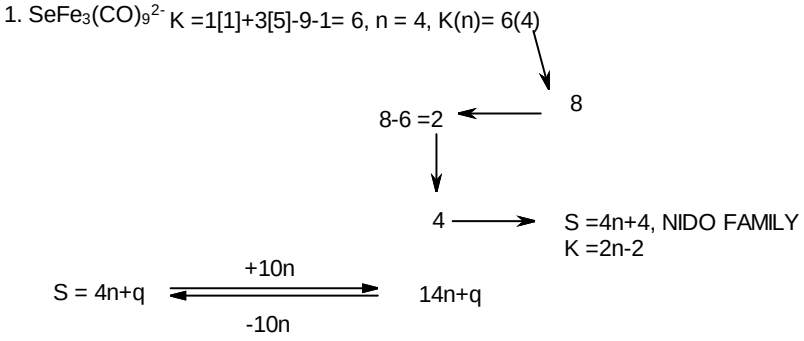
$Os_7(CO)_{21}$: K =7[5]-21 = 14, K(n) =14(7), S = 4n-0, Kp =C^1C[M6], [Mx] =[M6], Ve = 14+2x(x=6)+12(n-1) = 26+12(7-1) = 98, VF = 7[8]+42 = 98.

$Os_{10}(CO)_{26}^{2-}$: K =10[5]-26-1 = 23, K(n) =23(10), S = 4n-6, Kp =C^4C[M6], [Mx] =[M6], Ve = 14+2x(x=6)+12(n-1) = 26+12(10-1) =134, VF = 10[8]+26(2)+2 =134.

These calculations demonstrate that the capping principle based on series is valid.

2.6 The Generalized Capping Symbol, Kp = C^yC[Mx]

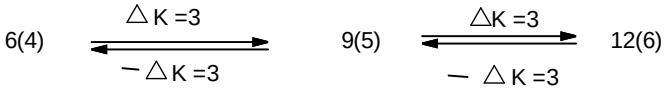
According to the series method approach, the series formula is given by S = 4n+q. The q can take up values, such as 10, 8, 6, ,4, , 2, , 0, - 2, -4, -6,-8, -10 and soon while x can have a mixture of even and odd numbers. It has been observed that the capping commences with series in which q≤0 and de-capping clusters are those in which q≥2. For example, a cluster with K= 12(6), S = 4n+0, K=2n+0, Kp=C^1C[M5]is mono-capped is predicted to have an ideal shape of a trigonal bipyramid cluster which has one capping skeletal element. On the other hand K(n) = 9(5), S = 4n+2, K = 2n-1 is expected to have an ideal trigonal bipyramid without a capping element, Kp = C^0C[M5]. The cluster with K(n) = 6(4) is expected to possess an ideal tetrahedral shape. This is what is observed for clusters shown in Schemes 4A and 4B. If we monitor the sequence of the K(n) values, 6(4)→9(5)→12(6), then the corresponding general capping symbols, Kp = $C^{-1}C$[M5]→ C^0C[M5]→ C^1C[M5] make sense as follows, $C^{-1}C$[M5] is a cluster one skeletal element before the closo shape, C^0C[M5] and C^1C[M5]is one skeletal element added to the ideal trigonal bipyramid closo symmetry. This is what is illustrated in Scheme 4A and 4B and typical examples given in Scheme 5. With this approach, the clusters with symmetries before the closo symmetry(C^{-y}) and after the closo symmetry(C^{+y}) baseline can readily be categorized.

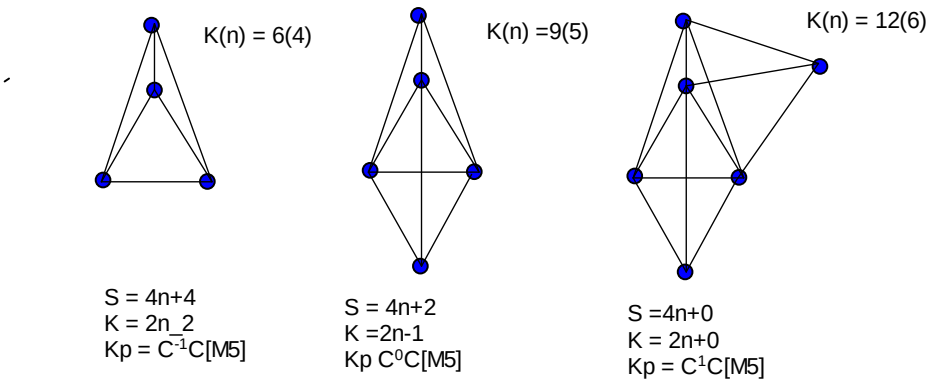


V = 4n+4 +10n = 4(4)+4+10(3) =50;VF =1[6]+3[8]+9(2)+2 =50;
V= adjusted valence electrons of the cluster,VF =valence elecrons from the cluster formula.

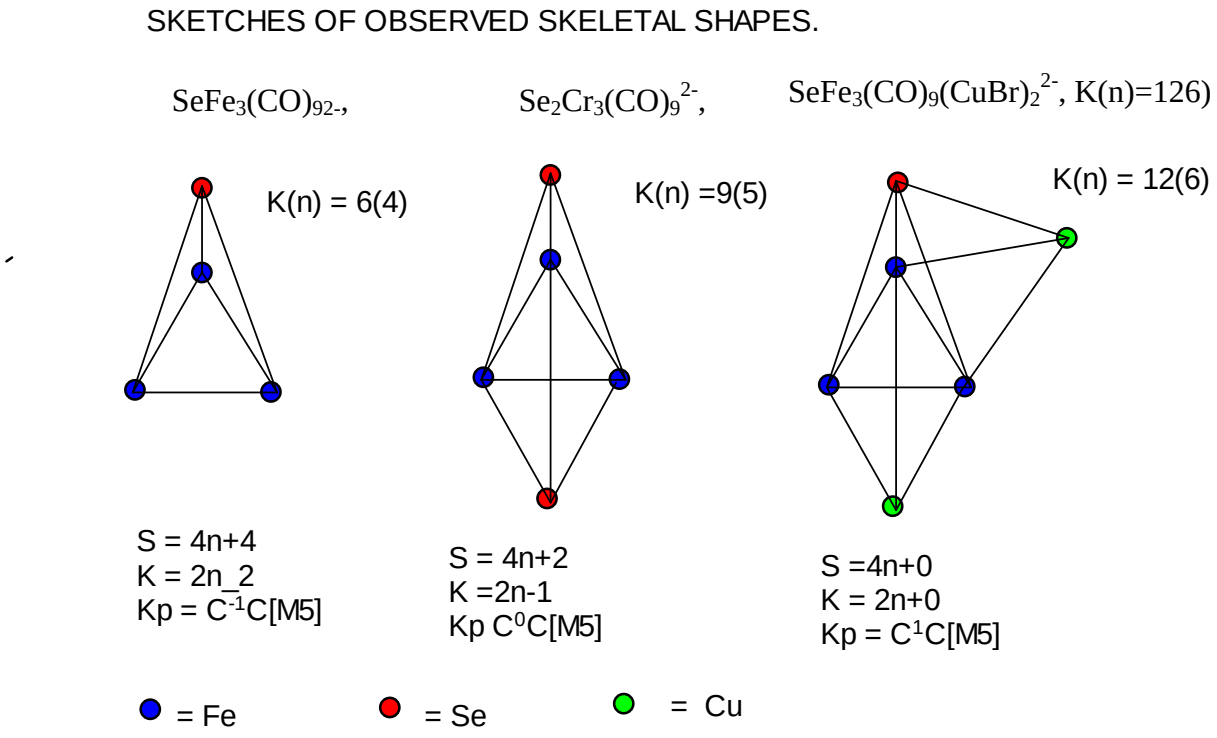
2. $Se_2Cr_3(CO)_{10}^{2-}$: K = 2[1]+3[6]-10-1 = 9, n = 5, K(n) = 9(5), S =4n+2,K= 2n-1
Kp = C^0C[M5], V = 4n+2+3(10) = 4(5)+2+30 = 52; VF = 2[6]+3[6]+10(2)+2 = 52

3. $SeFe_3(CO)_9(CuBr)_2^{2-}$:K=1[1]+3[5]-9+2[3.5-0.5]-1 =12, n =6, K(n) = 12(6); S = 4n+0,
K =2n+0, Kp=C^1C[M5]
V= 4n+0 +5(10) = 4(6)+0 +50 =74; VF = 1[6]+3[8]+9(2)+2[11+1]+2 =74





Scheme 4B. Examples of capping clusters of [M5] cluster clan



Scheme 5. Sketches of typical capping members of [M5] clan

2.7 Categorization of Clusters Into Groups of Clans and Families

In previous work, it was found that a given K(n) parameter can belong to any of the three main types of series, namely, those which follow the steps (ΔK = ±3, and Δn = ±1); (ΔK = ±2 and Δn =±1); and (ΔK = ±3, and Δn = 0). Numerical analysis of Rudolph system of categorization of borane clusters (Rudolph, 1976**)** reveals that the system worked according to the cluster series (ΔK = ±3, and Δn = ±1). The system has been found to be very useful for adoption to numerically categorize cluster series into FAMILIES and CLANS. A wide range of clusters have been compiled and categorized according to the Rudolph type of [Mx] cluster clans and are presented in Table 9. We can numerically illustrate this by the following K(n) values: 2(3)→5(4)→8(5) →11(6) →14(7) →17(8) →20(9) →23(10) →26(11) →29(12) →32(13) →35(14) →38(15) →41(16) →44(17) →47(18) →50(19) →53(20) →56(21) →59(22) →62(23) →65(24) →68(25) →71(26) →74(27) →77(28) →80(29) →83(30) →86(31) →89(32) →92(33) →95(34) →98(35) →101(36) →104(37) → 107(38) →110(39) →113(40) →116(41) →119(42) →122(43) →125(44), and so on. Since the closo K(n) parameter of all these series is 11(6), we can refer to this clam as the [M6]. The selected members of the [M6] clan are presented in Table 10 and fall within this range of the K(n) series. Part of this numerical series is highlighted in Table3. The corresponding series and the possible geometrical shapes are shown in the Scheme 3. Since the meeting point of capping ($C^yC[Mx]$) and uncapping cluster series ($C^{-y}C[Mx]$) is at [M6], S =4n+2 and K = 2n-1, these corresponding sets of K(n) member families may be regarded as [M6] CLAN. The clan includes all the K(n) families associated with [M6] reference point as well as K(n) = 11(6) family members**.**. Most of the CLUSTER CLANS are found within the range [M0] to [M12]. The members of [M6] CLAN itself have been extracted from Table 4 and are presented separately in Table10 as an illustration of a CLUSTER CLAN. The cluster families of [M6] range from K(n)=2(3) to K(n) = 125(44)as indicated in Table 9. In other words, the K values range from K = 2 to 125 for this family of [M6] which is also a subset of [M6] clan. The arrow in Table 3 indicates the K(n) parameters that are linking up the [M6] clan members. In principle, a single K(n) parameter represents one set of cluster family members. Hence, the sets of K(n) parameters that lie along a diagonal similar to those illustrated by the arrows represent given clan code-named by the corresponding nuclearity index of the corresponding closo clusters. Also highlighted in Table 3 are the K(n) series of CLAN MEMBERS of [M1] and [M2] as well as [M6].

Table 9. Categorization of Clusters and Elements into Clans and Families

CLUSTER	K(n)	SERIES S =4n+q	K(n) SERIES K =2n- ½ q	Kp =$C^yC[Mx]$	Ve= 18n-2K or 8n-2K
$Au_{102}R_{44}$	335(102)	4n-262	2n+131	$C^{132}C$[M-30]	1166
$Au_{40}R_{24}$	128(40)	4n-96	2n+48	$C^{49}C$[M-9]	464

$Au_{39}L_{14}Cl_6^{3+}$	121(39)	4n-86	2n+43	$C^{44}C$[M-5]	460
Ti	7(1)	4n-10	2n+5	$C^{6}C$[M-5]	4
Cr	6(1)	4n-8	2n+4	$C^{5}C$[M-4]	6
$Pd_{16}(CO)_7L_6$	51(16)	4n-38	2n+19	$C^{20}C$[M-4]	186
$Au_{39}L_{14}Cl_6^{+1}$	120(39)	4n-84	2n+42	$C^{43}C$[M-4]	462
Fe	5(1)	4n-6	2n+3	$C^{4}C$[M-3]	8
$Au_{38}L_{18}Cl_2^{4+}$	116(38)	4n-80	2n+40	$C^{41}C$[M-3]	452
Ni	4(1)	4n-4	2n+2	$C^{3}C$[M-2]	10
$Au_{25}L_{10}(SR)_5^{2+}$	76(25)	4n-52	2n+26	$C^{27}C$[M-2]	298
$Au_{36}R_{34}$	109(36)	4n-74	2n+37	$C^{38}C$[M-2]	430
Zn	3(1)	4n-2	2n+1	$C^{2}C$[M-1]	12
$Au_{10}L_3R_4$	30(10)	4n-20	2n+10	$C^{11}C$[M-1]	120
C	2(1)	4n+0	2n+0	$C^{1}C$[M0]	4
$Au_{20}L_{10}Cl_4^{2+}$	59(20)	4n-38	2n+19	$C^{20}C$[M0]	242
$Os_{20}(CO)_{40}^{2-}$	59(20)	4n-38	2n+19	$C^{20}C$[M0]	242
$Au_{22}L_{12}$	65(22)	4n-42	2n+21	$C^{22}C$[M0]	266
$Au_{24}L_{10}R_5X_2^{+1}$	71(24)	4n-46	2n+23	$C^{24}C$[M0]	290
O	1(1)	4n+2	2n-1	$C^{0}C$[M1]	6
S	1(1)	4n+2	2n-1	$C^{0}C$[M1]	6
BH_3	1(1)	4n+2	2n-1	$C^{0}C$[M1]	6
C_2	4(2)	4n+0	2n+0	$C^{1}C$[M1]	8
$Au_6L_6^{2+}$	16(6)	4n-8	2n+4	$C^{5}C$[M1]	76
$Au_8L_7^{2+}$	22(8)	4n-12	2n+6	$C^{7}C$[M1]	100
$Au_9L_8^{3+}$, L=PAr_3	25(9)	4n-14	2n+7	$C^{8}C$[M1]	112
$Au_{10}L_6Cl_3^{+}$	28(10)	4n-16	2n+8	$C^{9}C$[M1]	124
$V(CO)_6^{-}$	0(1)	4n+4	2n-2	$C^{-1}C$[M2]	18
$Cr(CO)_6$	0(1)	4n+4	2n-2	$C^{-1}C$[M2]	18
$Mn(CO)_6^{+}$	0(1)	4n+4	2n-2	$C^{-1}C$[M2]	18
$Fe(CO)_5$	0(1)	4n+4	2n-2	$C^{-1}C$[M2]	18
$Ru(CO)_5$	0(1)	4n+4	2n-2	$C^{-1}C$[M2]	18
$Os(CO)_5$	0(1)	4n+4	2n-2	$C^{-1}C$[M2]	18
$Os(CO)_6^{2+}$	0(1)	4n+4	2n-2	$C^{-1}C$[M2]	18
$Ir(CO)_6^{3+}$	0(1)	4n+4	2n-2	$C^{-1}C$[M2]	18
$Ni(CO)_4$	0(1)	4n+4	2n-2	$C^{-1}C$[M2]	18
CH_4	0(1)	4n+4	2n-2	$C^{-1}C$[M2]	8
PH_3	0(1)	4n+4	2n-2	$C^{-1}C$[M2]	8
OH_2	0(1)	4n+4	2n-2	$C^{-1}C$[M2]	8
$Co(CO)_4^{-}$	0(1)	4n+4	2n-2	$C^{-1}C$[M2]	18
NH_2^{-}	0(1)	4n+4	2n-2	$C^{-1}C$[M2]	8
$Mn(CO)_5^{-}$	0(1)	4n+4	2n-2	$C^{-1}C$[M2]	18
$(Cp)_2Co^{+}$	0(1)	4n+4	2n-2	$C^{-1}C$[M2]	18
(Cp)Ni(NO)	0(1)	4n+4	2n-2	$C^{-1}C$[M2]	18
$(Cp)Mn(CO)_3$	0(1)	4n+4	2n-2	$C^{-1}C$[M2]	18
$HFe(CO)_4^{-}$	0(1)	4n+4	2n-2	$C^{-1}C$[M2]	18
ReH_9^{2-}	0(1)	4n+4	2n-2	$C^{-1}C$[M2]	18
$Cr_2Cp_2(CO)_4$	3(2)	4n+2	2n-1	$C^{0}C$[M2]	30
N_2	3(2)	4n+2	2n-1	$C^{0}C$[M2]	10
P_2	3(2)	4n+2	2n-1	$C^{0}C$[M2]	10
$Mo_2Cp_2(CO)_4$	3(2)	4n+2	2n-1	$C^{0}C$[M2]	30
C_2H_2	3(2)	4n+2	2n-1	$C^{0}C$[M2]	10
C_3	6(3)	4n+0	2n+0	$C^{1}C$[M2]	12
$Pd_3(CO)_3L_3$	6(3)	4n+0	2n+0	$C^{1}C$[M2]	42
$Au_3L_3X_3$	6(3)	4n+0	2n+0	$C^{1}C$[M2]	42
$(AuL)_2Fe(CO)_4$	6(3)	4n+0	2n+0	$C^{1}C$[M2]	42
$Au_4I_2L_4$	9(4)	4n-2	2n+1	$C^{2}C$[M2]	54
$(AuL)_3O^{+}$	9(4)	4n-2	2n+1	$C^{2}C$[M2]	54
$(AuL)_3V(CO)_5$	9(4)	4n-2	2n+1	$C^{2}C$[M2]	54
$(AuL)_3Co(CO)_3$	9(4)	4n-2	2n+1	$C^{2}C$[M2]	54
$(AuL)_3Fe(CO)_4^{+}$	9(4)	4n-2	2n+1	$C^{2}C$[M2]	54
$Au_4L_4I_2$	9(4)	4n-2	2n+1	$C^{2}C$[M2]	54
$Fe_2Ir_2(AuL)(CO)_{12}^{+}$	12(5)	4n-4	2n+2	$C^{3}C$[M2]	66
$(AuL)_4Re(CO)_4^{+}$	12(5)	4n-4	2n+2	$C^{3}C$[M2]	66
$(AuL)_4Co(CO)_3^{+}$	12(5)	4n-4	2n+2	$C^{3}C$[M2]	66
$(AuL)_4Mn(CO)_4^{+}$	12(5)	4n-4	2n+2	$C^{3}C$[M2]	66
$(AuL)_4Re(CO)_4^{+}$	12(5)	4n-4	2n+2	$C^{3}C$[M2]	66
$(AuL)_5Fe(CO)_3^{+}$	15(6)	4n-6	2n+3	$C^{4}C$[M2]	78
$Au_8L_8^{2+}$	21(8)	4n-10	2n+5	$C^{6}C$[M2]	70

$(AuL)_7Mo(CO)_3^+$	21(8)	4n-10	2n+5	$C^6C[M2]$	102
$(AuL)_7Co(CO)_2^{2+}$	21(8)	4n-10	2n+5	$C^6C[M2]$	102
$Au_9L_8^+$	24(9)	4n-12	2n+6	$C^7C[M2]$	114
$(AuL)_8Pt(CO)^{2+}$	24(9)	4n-12	2n+6	$C^7C[M2]$	114
$Au_{10}L_8Cl^+$	27(10)	4n-14	2n+7	$C^8C[M2]$	126
$(AuL)_6(AuCl)_3Pt(CO)$	27(10)	4n-14	2n+7	$C^8C[M2]$	126
$Au_{11}L_7X_3$, L=PAr_3	30(11)	4n-16	2n+8	$C^9C[M2]$	138
$Au_{11}L_8Cl_2^+$	30(11)	4n-16	2n+8	$C^9C[M2]$	138
$Au_{11}L_{10}^{3+}$	30(11)	4n-16	2n+8	$C^9C[M2]$	138
$Au_{12}L_{10}Cl^{3+}$	33(12)	4n-18	2n+9	$C^{10}C[M2]$	150
$Au_{13}L_{10}Cl_2^{3+}$	36(13)	4n-20	2n+10	$C^{11}C[M2]$	162
$Au_{13}L_8Cl_4^+$	36(13)	4n-20	2n+10	$C^{11}C[M2]$	162
$Au_{13}L_7Cl_5$	36(13)	4n-20	2n+10	$C^{11}C[M2]$	162
$Au_{13}L_{10}Cl_2^{3+}$	36(13)	4n-20	2n+10	$C^{11}C[M2]$	162
$Au_{13}L_{12}^{5+}$	36(13)	4n-20	2n+10	$C^{11}C[M2]$	162
$Pd_{37}(CO)_{28}L_{12}$	108(37)	4n-68	2n+34	$C^{35}C[M2]$	450
$Re_2H_2(CO)_8$	2(2)	4n+4	2n-2	$C^{-1}C[M3]$	32
B_2H_6	2(2)	4n+4	2n-2	$C^{-1}C[M3]$	12
Bi_2^{2-}	2(2)	4n+4	2n-2	$C^{-1}C[M3]$	12
O_2	2(2)	4n+4	2n-2	$C^{-1}C[M3]$	12
S_2	2(2)	4n+4	2n-2	$C^{-1}C[M3]$	12
C_2H_4	2(2)	4n+4	2n-2	$C^{-1}C[M3]$	12
$Re_4H_4(CO)_{12}$	8(4)	4n+0	2n+0	$C^1C[M3]$	56
$SeMn_3(CO)_9^-$	8(4)	4n+0	2n+0	$C^1C[M3]$	56
$Au_8L_8Cl_2^{2+}$	20(8)	4n-8	2n+4	$C^5C[M3]$	104
$Au_{11}L_8Cl_3$	29(11)	4n-14	2n+7	$C^8C[M3]$	140
$Au_{16}L_8X_8$	44(16)	4n-24	2n+12	$C^{13}C[M3]$	200
$Au_6L_8^{2+}$	14(6)	4n-4	2n+2	$C^3C[M3]$	80
$(Cp^*Re)_2B_4H_4$	14(6)	4n-4	2n+2	$C^3C[M3]$	80
$Au_{15}L_{12}Cl(H)^{3+}$	41(15)	4n-22	2n+11	$C^{12}C[M3]$	188
$Cr_2Cp_2(NO)_4$	1(2)	4n+6	2n-3	$C^{-2}C[M4]$	34
$Mo_2Cp_2(CO)_6$	1(2)	4n+6	2n-3	$C^{-2}C[M4]$	34
$Mn_2(CO)_{10}$	1(2)	4n+6	2n-3	$C^{-2}C[M4]$	34
$Tc_2(CO)_{10}$	1(2)	4n+6	2n-3	$C^{-2}C[M4]$	34
$Re_2(CO)_{10}$	1(2)	4n+6	2n-3	$C^{-2}C[M4]$	34
$Re_2(Cp)_2(CO)_5$	1(2)	4n+6	2n-3	$C^{-2}C[M4]$	34
$Re_2H_3(CO)_8^-$	1(2)	4n+6	2n-3	$C^{-2}C[M4]$	34
C_2H_6	1(2)	4n+6	2n-3	$C^{-2}C[M4]$	34
$Co_2(CO)_8$	1(2)	4n+6	2n-3	$C^{-2}C[M4]$	34
$Fe_2(CO)_9$	1(2)	4n+6	2n-3	$C^{-2}C[M4]$	34
$Os_2(CO)_8^{2-}$	1(2)	4n+6	2n-3	$C^{-2}C[M4]$	34
$Os_2(Cp)_2(CO)_4$	1(2)	4n+6	2n-3	$C^{-2}C[M4]$	34
F_2	1(2)	4n+6	2n-3	$C^{-2}C[M4]$	14
$MoRuCp_2(CO)_5$	1(2)	4n+6	2n-3	$C^{-2}C[M4]$	34
$(Cp)_2Mo_2Fe(CO)_8$	4(3)	4n+4	2n-2	$C^{-1}C[M4]$	46
C_3H_4	4(3)	4n+4	2n-2	$C^{-1}C[M4]$	16
$Os_3H_2(CO)_{10}$	4(3)	4n+4	2n-2	$C^{-1}C[M4]$	46
$Re_3H_3(CO)_{10}^{2-}$	4(3)	4n+4	2n-2	$C^{-1}C[M4]$	46
$Re_3H_4(CO)_{10}^-$	4(3)	4n+4	2n-2	$C^{-1}C[M4]$	46
C_4H_2	7(4)	4n+2	2n-1	$C^0C[M4]$	18
$Re_4H_5(CO)_{12}^-$	7(4)	4n+2	2n-1	$C^0C[M4]$	58
C_5	10(5)	4n+0	2n+0	$C^1C[M4]$	20
$Au_{11}L_{12}^{3+}$	28(11)	4n-12	2n+6	$C^7C[M4]$	142
$Pt_{19}(CO)_{22}^{4-}$	52(19)	4n-28	2n+14	$C^{15}C[M4]$	238
$Os_3(CO)_{12}$	3(3)	4n+6	2n-3	$C^{-2}C[M5]$	48
$Re_3(H)(CO)_{12}^{2-}$	3(3)	4n+6	2n-3	$C^{-2}C[M5]$	48
$Re_3(H)_3(CO)_{12}$	3(3)	4n+6	2n-3	$C^{-2}C[M5]$	48
B_3H_9	3(3)	4n+6	2n-3	$C^{-2}C[M5]$	18
Bi_3^{3-}	3(3)	4n+6	2n-3	$C^{-2}C[M5]$	18
C_3H_6	3(3)	4n+6	2n-3	$C^{-2}C[M5]$	18
$Ru_3(CO)_{11}^{2-}$	3(3)	4n+6	2n-3	$C^{-2}C[M5]$	48
$Fe_3(CO)_{12}$	3(3)	4n+6	2n-3	$C^{-2}C[M5]$	48
$Ru_3(CO)_{12}$	3(3)	4n+6	2n-3	$C^{-2}C[M5]$	48
$Pd_{16}(CO)_{13}L_9$	42(16)	4n-20	2n+10	$C^{11}C[M5]$	204
$Os_2(CO)_{10}$	0(2)	4n+8	2n-4	$C^{-3}C[M5]$	36
P_4	6(4)	4n+4	2n-2	$C^{-1}C[M5]$	20
Pb_4^{4-}	6(4)	4n+4	2n-2	$C^{-1}C[M5]$	20

$Pb_2Sb_2^{2-}$	6(4)	4n+4	2n-2	$C^{-1}C[M5]$	20
$Sn_2Bi_2^{2-}$	6(4)	4n+4	2n-2	$C^{-1}C[M5]$	20
$Mn(CO)_3(B_3H_8)$	6(4)	4n+4	2n-2	$C^{-1}C[M5]$	30
C_4H_4	6(4)	4n+4	2n-2	$C^{-1}C[M5]$	20
$Co_4(CO)_{12}$	6(4)	4n+4	2n-2	$C^{-1}C[M5]$	60
$Rh_4(CO)_{12}$	6(4)	4n+4	2n-2	$C^{-1}C[M5]$	60
$Os_4(CO)_{14}$	6(4)	4n+4	2n-2	$C^{-1}C[M5]$	60
$Fe_4(CO)_{13}^{2-}$	6(4)	4n+4	2n-2	$C^{-1}C[M5]$	60
$Re_4H_4(CO)_{13}^{2-}$	6(4)	4n+4	2n-2	$C^{-1}C[M5]$	60
$Re_4H_6(CO)_{12}^{2-}$	6(4)	4n+4	2n-2	$C^{-1}C[M5]$	60
$InBi_3^{2-}$	6(4)	4n+4	2n-2	$C^{-1}C[M5]$	20
$Ir_4(CO)_{12}$	6(4)	4n+4	2n-2	$C^{-1}C[M5]$	60
$Pb_2Sb_2^{2-}$	6(4)	4n+4	2n-2	$C^{-1}C[M5]$	60
$S_2Fe_2(CO)_6$	6(4)	4n+4	2n-2	$C^{-1}C[M5]$	40
$TeFe_3(CO)_9^{2-}$	6(4)	4n+4	2n-2	$C^{-1}C[M5]$	50
$Os_5(CO)_{16}$	9(5)	4n+2	2n-1	$C^{-0}C[M5]$	72
$Se_2Cr_3(CO)_{10}^{2-}$	9(5)	4n+2	2n-1	$C^{-0}C[M5]$	52
$IrRu_3(CO)_{13}(AuL)$	9(5)	4n+2	2n-1	$C^{-0}C[M5]$	72
Bi_5^{3+}	9(5)	4n+2	2n-1	$C^{-0}C[M5]$	22
Sn_5^{2-}	9(5)	4n+2	2n-1	$C^{-0}C[M5]$	22
$Os_6(CO)_{18}$	12(6)	4n+0	2n+0	$C^{1}C[M5]$	84
$(Cp^*Re)_2B_4H_8$	12(6)	4n+0	2n+0	$C^{1}C[M5]$	44
$SeFe_3(CO)_9(CuBr)_2^{2-}$	12(6)	4n+0	2n+0	$C^{1}C[M5]$	74
C_6	12(6)	4n+0	2n+0	$C^{1}C[M5]$	24
$Pd_8(CO)_{10}L_4$	18(8)	4n-4	2n+2	$C^{3}C[M5]$	108
$Rh_{14}(CO)_{26}^{2-}$	36(14)	4n-16	2n+8	$C^{9}C[M5]$	180
$Rh_{15}(CO)_{27}^{3-}$	39(15)	4n-18	2n+9	$C^{10}C[M5]$	192
$Rh_{17}(CO)_{30}^{3-}$	45(17)	4n-22	2n+11	$C^{12}C[M5]$	216
$Re_3H_2(CO)_{13}^{-}$	2(3)	4n+8	2n-4	$C^{-3}C[M6]$	50
$Re_3H_3(CO)_{14}$	2(3)	4n+8	2n-4	$C^{-3}C[M6]$	50
$TeCr_2(CO)_{10}^{2-}$	2(3)	4n+8	2n-4	$C^{-3}C[M6]$	40
Te_4^{2+}	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	22
C_4H_6	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	22
B_4H_{10}	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	22
$Re_4(CO)_{16}^{2-}$	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	62
$Re_4H_5(CO)_{14}^{-}$	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	62
$Mn(CO)_4(B_3H_8)$	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	32
$(Cp^*Ir)B_3H_9$	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	32
Bi_4^{2-}	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	22
$Fe_4(C)(CO)_{13}$	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	62
$Fe_4(C)(CO)_{12}^{2-}$	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	62
$Fe_4(N)(CO)_{12}^{-}$	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	62
$Re_5(C)(CO)_{16}(H)^{2-}$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	74
$Fe_5(C)(CO)_{15}$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	74
$Fe_5(C)(CO)_{14}^{2-}$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	74
$Os_5(C)(CO)_{14}^{2-}$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	74
$Os_5(C)(CO)_{15}$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	74
$Fe_5(N)(CO)_{14}^{-}$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	74
$Fe_5(C)(CO)_{12}L_3$, L=PMe_2Ph	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	74
$C_2B_3H_7$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	24
$(CpRu)_2B_3H_9$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	44
$C_4H_4Fe(CO)_3$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	34
B_5H_9	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	24
$S_2Fe_3(CO)_9$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	54
$B_4H_8Fe(CO)_3$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	34
$B_4H_8(CoCp)$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	34
$B_4H_6(CoCp)_2$	11(6)	4n+2	2n-1	$C^{0}C[M6]$	46
C_6H_2	11(6)	4n+2	2n-1	$C^{0}C[M6]$	26
$Ru_6(CO)_{18}^{2-}$	11(6)	4n+2	2n-1	$C^{0}C[M6]$	86
$Ru_6(C)(CO)_{16}^{2-}$	11(6)	4n+2	2n-1	$C^{0}C[M6]$	86
$Ru_6(C)(CO)_{17}$	11(6)	4n+2	2n-1	$C^{0}C[M6]$	86
$Ru_6(C)(CO)_{16}(L)$, L=PPh_2Et	11(6)	4n+2	2n-1	$C^{0}C[M6]$	86
$Ru_6(CO)_{17}(B)^{-}$	11(6)	4n+2	2n-1	$C^{0}C[M6]$	86
$Co_8(C)(CO)_{18}^{2-}$	15(8)	4n+2	2n-1	$C^{0}C[M8]$	86
$Re_8(C)(CO)_{24}^{2-}$	17(8)	4n-2	2n+1	$C^{2}C[M6]$	86
$Os_8(CO)_{22}^{2-}$	17(8)	4n-2	2n+1	$C^{2}C[M6]$	86
$Os_6(CO)_{18}^{2-}$	11(6)	4n+2	2n-1	$C^{0}C[M6]$	86

$Re_6(C)(CO)_{19}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Re_6(C)(CO)_{19}H^-$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Re_6(C)(CO)_{18}H^{3-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Re_6(C)(CO)_{18}H_2^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Re_6(H)_7(CO)_{18}^-$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Co_6(CO)_{16}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Rh_6(CO)_{16}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Ir_6(CO)_{16}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$B_6H_6^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	26
$(CpCo)_3B_3H_5$	11(6)	4n+2	2n-1	$C^0C[M6]$	56
$Se_2Mn_4(CO)_{12}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	66
$Fe_6(C)(CO)_{16}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Fe_6Rh(N)(CO)_{15}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Fe_4Rh_2(N)(CO)_{15}^-$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Fe_6(N)(CO)_{15}^{3-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Ni_6(CO)_{12}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$(Cp^*Ru)_2B_4H_8$	11(6)	4n+2	2n-1	$C^0C[M6]$	46
$(CpCo)_3B_3H_5$	11(6)	4n+2	2n-1	$C^0C[M6]$	56
$(Cp^*Ru)_3B_3H_8$	11(6)	4n+2	2n-1	$C^0C[M6]$	56
$C_2B_4H_6$	11(6)	4n+2	2n-1	$C^0C[M6]$	26
$(CpCo)_2B_4H_6$	11(6)	4n+2	2n-1	$C^0C[M6]$	46
$C_2B_3H_5Fe(CO)_3$	11(6)	4n+2	2n-1	$C^0C[M6]$	36
$SFe_2Ru_3(CO)_{14}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	76
$Fe_3Pt_3(CO)_{15}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Te_2Ru_4(CO)_{10}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	66
$Se_2Mn_4(CO)_{12}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	66
$Os_7(CO)_{21}$	14(7)	4n+0	2n+0	$C^1C[M6]$	98
$Re_7(C)(CO)_{21}^{3-}$	14(7)	4n+0	2n+0	$C^1C[M6]$	98
$Re_7(C)(CO)_{21}H^{2-}$	14(7)	4n+0	2n+0	$C^1C[M6]$	98
$Re_7(C)(CO)_{21}H_2^-$	14(7)	4n+0	2n+0	$C^1C[M6]$	98
$Re_7(C)(CO)_{22}^-$	14(7)	4n+0	2n+0	$C^1C[M6]$	98
$TeRu_5(CO)_{14}(CuCl)^{2-}$	14(7)	4n+0	2n+0	$C^1C[M6]$	68
$Re_8(C)(CO)_{24}^{2-}$	17(8)	4n-2	2n+1	$C^2C[M6]$	110
$Os_8(CO)_{22}^{2-}$	17(8)	4n-2	2n+1	$C^2C[M6]$	110
$Pd_{10}(CO)_{12}L_6$	22(10)	4n-6	2n+3	$C^4C[M6]$	136
$Rh_{10}(CO)_{21}^{2-}$	23(10)	4n-6	2n+3	$C^4C[M6]$	134
$Ru_{10}(C)(CO)_{24}^{2-}$	23(10)	4n-6	2n+3	$C^4C[M6]$	134
$Os_{10}(C)(CO)_{24}^{2-}$	23(10)	4n-6	2n+3	$C^4C[M6]$	134
$Os_{10}(H)(C)(CO)_{24}^-$	23(10)	4n-6	2n+3	$C^4C[M6]$	134
$Os_{10}(H)_4(CO)_{24}^{2-}$	23(10)	4n-6	2n+3	$C^4C[M6]$	134
$(Cp^*Re)_2B_7H_7$	20(9)	4n-4	2n+2	$C^3C[M6]$	52
$Rh_9(CO)_{19}^{3-}$	20(9)	4n-4	2n+2	$C^3C[M6]$	122
$Os_9(CO)_{24}^{2-}$	20(9)	4n-4	2n+2	$C^3C[M6]$	122
$Ir_{12}(CO)_{24}^{2-}$	29(12)	4n-10	2n+5	$C^6C[M6]$	158
$Ru_6Pd_6(CO)_{24}^{2-}$	29(12)	4n-10	2n+5	$C^6C[M6]$	158
$Rh_{13}(CO)_{24}(H)^{4-}$	32(13)	4n-13	2n+6	$C^7C[M6]$	170
$Ni_{38}Pt_6(CO)_{48}^{6-}$	125(44)	4n-74	2n+37	$C^{38}C[M6]$	542
$Ni_{38}Pt_6(CO)_{48}(H)^{5-}$	125(44)	4n-74	2n+37	$C^{38}C[M6]$	542
$Pt_{38}(CO)_{44}^{2-}$	107(38)	4n-62	2n+31	$C^{32}C[M6]$	470
$C_2B_4H_6NiL_2$	13(7)	4n+2	2n-1	$C^0C[M7]$	40
$C_2B_3H_5(CoCp)_2$	13(7)	4n+2	2n-1	$C^0C[M7]$	50
$C_2B_4H_4(R_2Sn)(CoCp)$	13(7)	4n+2	2n-1	$C^0C[M7]$	40
$C_2B_4H_6NiL_2$	13(7)	4n+2	2n-1	$C^0C[M7]$	40
$C_2B_3H_5(CoCp)_2$	13(7)	4n+2	2n-1	$C^0C[M7]$	50
$C_2B_4H_4(R_2Sn)(CoCp)$	13(7)	4n+2	2n-1	$C^0C[M7]$	40
B_7H_9	13(7)	4n+2	2n-1	$C^0C[M7]$	30
$Co_7(N)(CO)_{15}^{2-}$	13(7)	4n+2	2n-1	$C^0C[M7]$	100
$Rh_7(N)(CO)_{15}^{2-}$	13(7)	4n+2	2n-1	$C^0C[M7]$	100
C_4H_8	4(4)	4n+8	2n-4	$C^{-3}C[M7]$	24
$Re_4H_4(CO)_{15}^{2-}$	4(4)	4n+8	2n-4	$C^{-3}C[M7]$	64
$Re_4H_4(CO)_{16}$	4(4)	4n+8	2n-4	$C^{-3}C[M7]$	64
$Rh_5(CO)_{15}^-$	7(5)	4n+6	2n-3	$C^{-2}C[M7]$	76
$Os_5(CO)_{18}$	7(5)	4n+6	2n-3	$C^{-2}C[M7]$	76
B_5H_{11}	7(5)	4n+6	2n-3	$C^{-2}C[M7]$	26
C_5H_6	7(5)	4n+6	2n-3	$C^{-2}C[M7]$	26
$Fe_4(Au)(CO)_{16}^{2-}$	7(5)	4n+6	2n-3	$C^{-2}C[M7]$	76
$Fe_4(Pt)(CO)_{16}^{2-}$	7(5)	4n+6	2n-3	$C^{-2}C[M7]$	76

C_6H_4	10(6)	4n+4	2n-2	$C^{-1}C[M7]$	28
B_6H_{10}	10(6)	4n+4	2n-2	$C^{-1}C[M7]$	28
$C_2B_4H_8$	10(6)	4n+4	2n-2	$C^{-1}C[M7]$	28
$(CpFe)B_5H_{10}$	10(6)	4n+4	2n-2	$C^{-1}C[M7]$	38
$Re_6(H)_8(CO)_{18}^{2-}$	10(6)	4n+4	2n-2	$C^{-1}C[M7]$	88
$Rh_{12}(CO)_{25}(H)_2$	28(12)	4n-8	2n+4	$C^{5}C[M7]$	160
$Fe_6Pd_6(CO)_{24}(H)^{3-}$	28(12)	4n-8	2n+4	$C^{5}C[M7]$	160
$Rh_{11}(CO)_{23}^{3-}$	25(11)	4n-6	2n+3	$C^{4}C[M7]$	148
C_4H_{10}	3(4)	4n+10	2n-5	$C^{-4}C[M8]$	26
Te_4^{2-}	3(4)	4n+10	2n-5	$C^{-4}C[M8]$	26
Se_4^{2-}	3(4)	4n+10	2n-5	$C^{-4}C[M8]$	26
$TeCr_3(CO)_{15}^{2-}$	3(4)	4n+10	2n-5	$C^{-4}C[M8]$	56
C_5H_8	6(5)	4n+8	2n-4	$C^{-3}C[M8]$	28
$Os_5(CO)_{19}$	6(5)	4n+8	2n-4	$C^{-3}C[M8]$	78
C_6H_6	9(6)	4n+6	2n-3	$C^{-2}C[M8]$	30
$Os_6(CO)_{18}(P)^-$	9(6)	4n+6	2n-3	$C^{-2}C[M8]$	90
$Co_6(C)(CO)_{15}^{2-}$	9(6)	4n+6	2n-3	$C^{-2}C[M8]$	90
$Rh_6(C)(CO)_{15}^{2-}$	9(6)	4n+6	2n-3	$C^{-2}C[M8]$	90
$Co_6(N)(CO)_{15}^{2-}$	9(6)	4n+6	2n-3	$C^{-2}C[M8]$	90
$Rh_6(N)(CO)_{15}^-$	9(6)	4n+6	2n-3	$C^{-2}C[M8]$	90
$Co_6(C)_2(CO)_{15}^{2-}$	9(6)	4n+6	2n-3	$C^{-2}C[M8]$	90
P_6	9(6)	4n+6	2n-3	$C^{-2}C[M8]$	30
$Os_6L_4(CO)_{17}$	9(6)	4n+6	2n-3	$C^{-2}C[M8]$	90
$Os_6(CO)_{18}(P)^-$	9(6)	4n+6	2n-3	$C^{-2}C[M8]$	90
$Rh_6(CO)_{15}(N)^-$	9(6)	4n+6	2n-3	$C^{-2}C[M8]$	90
$Ni_6(Cp)_6$	9(6)	4n+6	2n-3	$C^{-2}C[M8]$	90
B_6H_{12}	9(6)	4n+6	2n-3	$C^{-2}C[M8]$	90
$B_8H_8^{2-}$	15(8)	4n+2	2n-1	$C^{0}C[M8]$	34
$Co_8(C)(CO)_{18}^{2-}$	15(8)	4n+2	2n-1	$C^{0}C[M8]$	114
$Bi_3Ni_6(CO)_6^{3-}$	18(9)	4n+0	2n+0	$C^{1}C[M8]$	96
$Ir_{12}(CO)_{26}^{2-}$	27(12)	4n-6	2n+3	$C^{4}C[M8]$	162
$Pd_{39}(CO)_{28}L_{12}$	106(39)	4n-56	2n+28	$C^{29}C[M8]$	490
$Pd_{33}(CO)_{28}L_{14}$	90(33)	4n-48	2n+24	$C^{25}C[M8]$	414
$Pd_{23}(CO)_{22}L_{10}$	60(23)	4n-28	2n+14	$C^{15}C[M8]$	294
C_5H_{10}	5(5)	4n+10	2n-5	$C^{-4}C[M9]$	30
$Co_6(C)_2(CO)_{15}^{2-}$	7(6)	4n+8	2n-4	$C^{-3}C[M9]$	94
C_6H_8	8(6)	4n+8	2n-4	$C^{-3}C[M9]$	32
$Co_6(P)(CO)_{16}^-$	8(6)	4n+8	2n-4	$C^{-3}C[M9]$	92
$(Cp^*Fe)B_4H_{11}$	5(7)	4n+6	2n-3	$C^{-2}C[M9]$	56
$C_2B_6H_8PtL_2$	17(9)	4n+2	2n-1	$C^{0}C[M9]$	48
$Pt_9(CO)_{18}^{2-}$	17(9)	4n+2	2n-1	$C^{0}C[M9]$	128
B_9H_{11}	17(9)	4n+2	2n-1	$C^{0}C[M9]$	38
Ge_9^{2-}	17(9)	4n+2	2n-1	$C^{0}C[M9]$	38
$TlSn_8^{3-}$	17(9)	4n+2	2n-1	$C^{0}C[M9]$	38
$Tl_5Sb_4^{3-}$	17(9)	4n+2	2n-1	$C^{0}C[M9]$	38
$Tl_6Sb_3^{5-}$	17(9)	4n+2	2n-1	$C^{0}C[M9]$	38
$C_2B_5H_7(CoCp)_2$	17(9)	4n+2	2n-1	$C^{0}C[M9]$	58
C_5H_{12}	4(5)	4n+12	2n-6	$C^{-5}C[M10]$	32
C_6H_{10}	7(6)	4n+10	2n-5	$C^{-4}C[M10]$	34
Te_4^{2+}	7(6)	4n+10	2n-5	$C^{-4}C[M10]$	34
$B_9H_9(NiCp)^-$	19(10)	4n+2	2n-1	$C^{0}C[M10]$	72
$CB_7H_8(CoCp)(NiCp)$	19(10)	4n+2	2n-1	$C^{0}C[M10]$	62
$Co_{11}(N)_2(CO)_{21}^{3-}$	22(11)	4n+0	2n+0	$C^{1}C[M10]$	154
$Co_{10}(Rh)(N)_2(CO)_{21}^{3-}$	22(11)	4n+0	2n+0	$C^{1}C[M10]$	154
$Rh_{12}(C)_2(CO)_{23}^{4-}$	25(12)	4n-2	2n+1	$C^{2}C[M10]$	266
$Rh_{12}(C)_2(CO)_{24}^{2-}$	25(12)	4n-2	2n+1	$C^{2}C[M10]$	266
$Ag_{13}Fe_8(CO)_{32}^{3-}$	52(21)	4n-20	2n+10	$C^{11}C[M10]$	274
$Pd_{20}Ni_{26}(CO)_{54}^{6-}$	127(46)	4n-70	2n+35	$C^{36}C[M10]$	574
P_4S_3	9(7)	4n+10	2n-5	$C^{-4}C[M11]$	38
As_7^{3-}	9(7)	4n+10	2n-5	$C^{-4}C[M11]$	38
Bi_7^{3-}	9(7)	4n+10	2n-5	$C^{-4}C[M11]$	38
B_9H_{15}	15(9)	4n+6	2n-3	$C^{-2}C[M11]$	42
Sn_9^{4-}	16(9)	4n+6	2n-3	$C^{-2}C[M11]$	40
$H_5Re_6(CO)_{24}^-$	6(6)	4n+12	*2n-6*	$C^{-5}C[M11]$	96
C_6H_{12}	6(6)	4n+12	2n-6	$C^{-5}C[M11]$	36
$B_{10}H_{14}$	18(10)	4n+4	2n-2	$C^{-1}C[M11]$	44
$B_{11}H_{13}$	21(11)	4n+2	2n-1	$C^{0}C[M11]$	46

$CB_9H_{10}(CoCp)^-$	21(11)	4n+2	2n-1	$C^0C[M11]$	56
$C_2B_8H_{10}Ir(H)L_2$	21(11)	4n+2	2n-1	$C^0C[M11]$	56
Tl_{13}^{11-}	27(13)	4n-2	2n+1	$C^2C[M11]$	50
$Fe_6Ni_6(CO)_{24}(N)_2^{2-}$	24(12)	4n+0	2n+0	$C^1C[M11]$	168
$Pd_{38}(CO)_{28}L_{12}$	102(38)	4n-52	2n+26	$C^{27}C[M11]$	480
$Rh_{12}(CO)_{30}^{2-}$	23(12)	4n+2	2n-1	$C^0C[M12]$	170
$Co_8Pt_4(C)_2(CO)_{24}^{2-}$	23(12)	4n+2	2n-1	$C^0C[M12]$	170
$B_{12}H_{14}$	23(12)	4n+2	2n-1	$C^0C[M12]$	50
$C_2B_7H_9(CoCp)_3$	23(12)	4n+2	2n-1	$C^0C[M12]$	80
$C_2B_9H_{11}Ru(CO)_3$	23(12)	4n+2	2n-1	$C^0C[M12]$	60
C_6H_{14}	5(6)	4n+14	2n-7	$C^{-6}C[M12]$	38
$Co_6(C)_2(CO)_{18}$	5(6)	4n+14	2n-7	$C^{-6}C[M12]$	98
P_4S_4	10(8)	4n+12	2n-6	$C^{-5}C[M13]$	44
$Co_{11}(N)_2(CO)_{24}^{3-}$	19(11)	4n+6	2n-3	$C^{-2}C[M13]$	160
P_4S_5	11(9)	4n+14	2n-7	$C^{-6}C[M15]$	50
P_4S_6	12(10)	4n+16	2n-8	$C^{-7}C[M17]$	56
$Ni_{38}(C)_6(CO)_{42}^{6-}$	95(38)	4n-38	2n+19	$C^{20}C[M18]$	494
$Ni_{32}(C)_6(CO)_{36}^{6-}$	77(32)	4n-26	2n+13	$C^{14}C[M18]$	422
Se_{10}^{2+}	11(10)	4n+18	2n-9	$C^{-8}C[M18]$	58
$Te_2Se_8^{2+}$	11(10)	4n+18	2n-9	$C^{-8}C[M18]$	58
P_4S_7	13(11)	4n+18	2n-9	$C^{-8}C[M19]$	62
P_4S_8	14(12)	4n+20	2n-10	$C^{-9}C[M21]$	68
P_4S_9	15(13)	4n+22	2n-11	$C^{-10}C[M23]$	74
$Te_8Fe_8(CO)_{24}^{2-}$	23(16)	4n+18	2n-9	$C^{-8}C[M24]$	162
P_4S_{10}	16(14)	4n+24	2n-12	$C^{-11}C[M25]$	80
P_{18}	27(18)	4n+18	2n-9	$C^{-8}C[M26]$	90
Se_{16}^{2+}	17(16)	4n+30	2n-15	$C^{-14}C[M30]$	94

Table 10. An illustration of an [M6] Cluster Clan and its Families

Typical cluster representative	K(n)	S=4n+q	K=2n- ½ q	Kp= $C^YC[Mx]$	Ve
$Re_3H_3(CO)_{14}$	2(3)	4n+8	2n-4	$C^{-3}C[M6]$	50
$TeCr_2(CO)_{10}^{2-}$	2(3)	4n+8	2n-4	$C^{-3}C[M6]$	40
Te_4^{2+}	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	22
C_4H_6	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	22
B_4H_{10}	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	22
$Re_4(CO)_{16}^{2-}$	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	62
$Re_4H_5(CO)_{14}^-$	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	62
$Mn(CO)_4(B_3H_8)$	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	32
$(Cp^*Ir)B_3H_9$	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	32
Bi_4^{2-}	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	22
$Fe_4(C)(CO)_{13}$	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	62
$Fe_4(C)(CO)_{12}^{2-}$	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	62
$Fe_4(N)(CO)_{12}^-$	5(4)	4n+6	2n-3	$C^{-2}C[M6]$	62
$Re_5(C)(CO)_{16}(H)^{2-}$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	74
$Fe_5(C)(CO)_{15}$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	74
$Fe_5(C)(CO)_{14}^{2-}$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	74
$Os_5(C)(CO)_{14}^{2-}$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	74
$Os_5(C)(CO)_{15}$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	74
$Fe_5(N)(CO)_{14}^-$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	74
$Fe_5(C)(CO)_{12}L_3$, L=PMe_2Ph	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	74
$C_2B_3H_7$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	24
$(CpRu)_2B_3H_9$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	44
$C_4H_4Fe(CO)_3$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	34
B_5H_9	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	24
$S_2Fe_3(CO)_9$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	54
$B_4H_8Fe(CO)_3$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	34
$B_4H_8(CoCp)$	8(5)	4n+4	2n-2	$C^{-1}C[M6]$	34
$B_4H_6(CoCp)_2$	11(6)	4n+2	2n-1	$C^0C[M6]$	46
C_6H_2	11(6)	4n+2	2n-1	$C^0C[M6]$	26
$Ru_6(CO)_{18}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Ru_6(C)(CO)_{16}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Ru_6(C)(CO)_{17}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Ru_6(C)(CO)_{16}(L)$, L=PPh_2Et	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Ru_6(CO)_{17}(B)^-$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Os_6(CO)_{18}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Re_6(C)(CO)_{19}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Re_6(C)(CO)_{19}H^-$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Re_6(C)(CO)_{18}H^{3-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86

$Re_6(C)(CO)_{18}H_2^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Re_6(H)_7(CO)_{18}^-$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Co_6(CO)_{16}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Rh_6(CO)_{16}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Ir_6(CO)_{16}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$B_6H_6^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	26
$(CpCo)_3B_3H_5$	11(6)	4n+2	2n-1	$C^0C[M6]$	56
$Se_2Mn_4(CO)_{12}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	66
$Fe_6(C)(CO)_{16}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Fe_6Rh(N)(CO)_{15}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Fe_4Rh_2(N)(CO)_{15}^-$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Fe_6(N)(CO)_{15}^{3-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Ni_6(CO)_{12}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$(Cp^*Ru)_2B_4H_8$	11(6)	4n+2	2n-1	$C^0C[M6]$	46
$(CpCo)_3B_3H_5$	11(6)	4n+2	2n-1	$C^0C[M6]$	56
$(Cp^*Ru)_3B_3H_8$	11(6)	4n+2	2n-1	$C^0C[M6]$	56
$C_2B_4H_6$	11(6)	4n+2	2n-1	$C^0C[M6]$	26
$(CpCo)_2B_4H_6$	11(6)	4n+2	2n-1	$C^0C[M6]$	46
$C_2B_3H_5Fe(CO)_3$	11(6)	4n+2	2n-1	$C^0C[M6]$	36
$SFe_2Ru_3(CO)_{14}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	76
$Fe_3Pt_3(CO)_{15}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	86
$Te_2Ru_4(CO)_{10}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	66
$Se_2Mn_4(CO)_{12}^{2-}$	11(6)	4n+2	2n-1	$C^0C[M6]$	66
$Os_7(CO)_{21}$	14(7)	4n+0	2n+0	$C^1C[M6]$	98
$Re_7(C)(CO)_{21}^{3-}$	14(7)	4n+0	2n+0	$C^1C[M6]$	98
$Re_7(C)(CO)_{21}H^{2-}$	14(7)	4n+0	2n+0	$C^1C[M6]$	98
$Re_7(C)(CO)_{21}H_2^-$	14(7)	4n+0	2n+0	$C^1C[M6]$	98
$Re_7(C)(CO)_{22}^-$	14(7)	4n+0	2n+0	$C^1C[M6]$	98
$TeRu_5(CO)_{14}(CuCl)^{2-}$	14(7)	4n+0	2n+0	$C^1C[M6]$	68
$Re_8(C)(CO)_{24}^{2-}$	17(8)	4n-2	2n+1	$C^2C[M6]$	110
$Os_8(CO)_{22}^{2-}$	17(8)	4n-2	2n+1	$C^2C[M6]$	110
$Re_8(C)(CO)_{24}^{2-}$	17(8)	4n-2	2n+1	$C^2C[M6]$	110
$Os_8(CO)_{22}^{2-}$	17(8)	4n-2	2n+1	$C^2C[M6]$	110
$(Cp^*Re)_2B_7H_7$	20(9)	4n-4	2n+2	$C^3C[M6]$	52
$Rh_9(CO)_{19}^{3-}$	20(9)	4n-4	2n+2	$C^3C[M6]$	122
$Os_9(CO)_{24}^{2-}$	20(9)	4n-4	2n+2	$C^3C[M6]$	122
$Pd_{10}(CO)_{12}L_6$	23(10)	4n-6	2n+3	$C^4C[M6]$	136
$Rh_{10}(CO)_{21}^{2-}$	23(10)	4n-6	2n+3	$C^4C[M6]$	134
$Ru_{10}(C)(CO)_{24}^{2-}$	23(10)	4n-6	2n+3	$C^4C[M6]$	134
$Os_{10}(C)(CO)_{24}^{2-}$	23(10)	4n-6	2n+3	$C^4C[M6]$	134
$Os_{10}(H)(C)(CO)_{24}^-$	23(10)	4n-6	2n+3	$C^4C[M6]$	134
$Os_{10}(H)_4(CO)_{24}^{2-}$	23(10)	4n-6	2n+3	$C^4C[M6]$	134
$Ir_{12}(CO)_{24}^{2-}$	29(12)	4n-10	2n+5	$C^6C[M6]$	158
$Ru_6Pd_6(CO)_{24}^{2-}$	29(12)	4n-10	2n+5	$C^6C[M6]$	158
$Rh_{13}(CO)_{24}(H)^{4-}$	32(13)	4n-13	2n+6	$C^7C[M6]$	170
$Pt_{38}(CO)_{44}^{2-}$	107(38)	4n-62	2n+31	$C^{32}C[M6]$	470
$Ni_{38}Pt_6(CO)_{48}^{6-}$	125(44)	4n-74	2n+37	$C^{38}C[M6]$	542
$Ni_{38}Pt_6(CO)_{48}(H)^{5-}$	125(44)	4n-74	2n+37	$C^{38}C[M6]$	542

Appendix. Skeletal Numbers of Main Group and Transition Metal Elements

K	7.5(1)	7(1)	6.5(1)	6(1)	5.5(1)	5(1)	4.5(1)	4(1)	3.5(1)	3(1)	2.5(1)	2(1)	1.5(1)	1(1)	0.5(1)	0(1)
3d	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn						
4d	Yb	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd						
5d	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg						
								2s	Li	Be	B	C	N	O	F	Ne
								3s	Na	Mg	Al	Si	P	S	Cl	Ar
								4s	K	Ca	Ga	Ge	As	Se	Br	Kr
								5s	Rb	Sr	In	Sn	Sb	Te	I	Xe
								6s	Cs	Ba	Tl	Pb	Bi	Po	At	Rn

3. Conclusion

A skeletal element or its cluster can be expressed by a single whole number referred to as K and is usually specified by adding n to it to produce the K(n) parameter where n represents the number of skeletal elements involved. However the series method has been confined to main group elements or transition metals. Every K(n) parameter represents a specific number of cluster valence electrons(Ve). The K(n) parameters form series and consequently their corresponding cluster valence electron contents do the same. An array of K(n) parameters can be regarded as a cluster map on which the cluster valence electron content of each skeletal element or cluster can be located. The application of three important formulas for calculating cluster valence electrons has been emphasized. A new formula based on capping series which is also important for calculating cluster valence electron content has been introduced for the first time. It has also been shown that the clusters and skeletal elements can broadly be categorized into families and clans based on their nuclear indices [Mx].

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