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The Capping Theory of Chemical Clusters Based on 12N/14N Series

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Abstract

The genesis of chemical clusters of the transition and main group elements has been established. The base-line for cluster valence electrons has been demarcated with help of capping series. Using the base-line as a reference, the formulas of fragments and clusters were generated. Also a simple general formula for calculating cluster valence electrons for systems ranging from a single to multi-skeletal element clusters was identified. The concepts of the existence of nuclei in clusters and some having black-holes were well established. The capping principle was extended to the main group and transition elements of the periodic table and a difference between metals and non-metals was discerned. The skeletal elements of clusters whose series have advanced beyond closo baseline level S=4n+2 can be separated into two broad groups, namely those which follow the closo series(nucleus) and those which follow the capping series.

Keywords: black-holes, cluster nucleus, baseline, matrix, clan series, family series, genesis, capping electrons, arithmetic progression

1. Introduction

The capping concept has been widely applied to explain certain features of clusters for sometime(Mingos, 1991; Driess & NÖth, 2004; Wales, 2005; Goicoechea & Sevov, 2006; Amela-Cortes, et al, 2014). The clusters that have been described as capped, among others include, $B_9H_9^{2-}$,tri-capped trigonal prism(Housecroft & Sharpe,2005); $Au_3Ru_4(CO)_{12}L_3(H)$, tri-capped tetrahedron(Teo & Longoni, 1984), and $Ru_6Pd_6(CO)_{24}^{2-}$, hexa-capped octahedron (Teo & Longoni, 1984); $Fe_6Pd_6(CO)_{24}(H)^{3-}$, hexa-capped octahedron(Teo &Longoni,1984); $Cu_{26}Se_{13}L_{14}$, body-centered icosahedron cluster(Crawford, et al, 2002); $Ga_{22}R_8$, a centered 13-vertex cluster with 8 cappings(Driess & NÖth, 2004) and $Au_{11}L_7I_3$(L=PR_3),one central golden atom surrounded by 10 others(Malatesta,1975). According to the 4N series approach, all skeletal elements from single to multi-skeletal clusters can be represented by a capping symbol Kp=$C^yC[Mx]$, where y+x= n(the number of skeletal elements). This capping method which has developed to a level of using skeletal numbers is quite easy, systematic and standardized (Kiremire 2017a). The skeletal numbers of the periodic table elements used in calculating the K(N) parameters of clusters are provided in Tables 7 and 8 for ease of reference. A new method of deriving cluster valence electrons and formulas has been developed in this paper and the capping principle based on the 12N/14N series demonstrated.

2. Results and Discussion

2.1 The Genesis of the Chemical Clusters

The capping principle of clusters is well revealed by considering the genesis of the cluster series. Let us illustrate this by focusing on [M6] clan series. The symbol represents 6 skeletal elements which are bound together and belong to the CLOSO family of clusters (Kiremire,2015a). This means that it is associated with the series S=4n+2, K=2n-1=2[6]-1=11, K(n)= 11(6). The cluster valence electrons are given by VE=4n+6= 4[6]+2=26 for the main group elements and VE= 14n+2=14[6]+2=86 for the transition metals. The ideal shape of the fragment is an octahedron as shown in Figure 1.

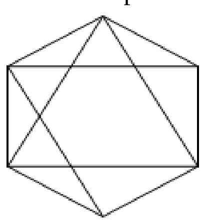
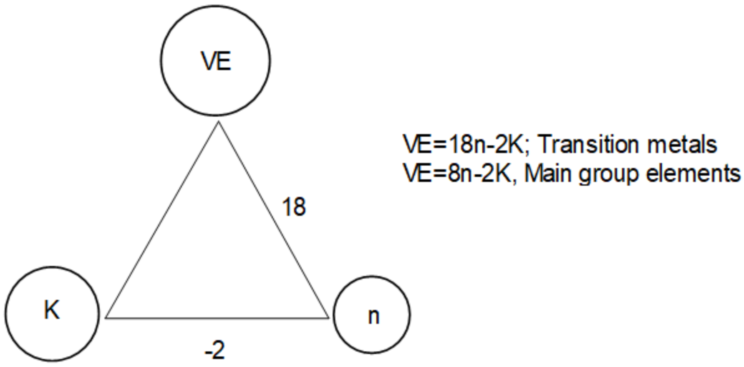


Figure 1. Ideal O_h geometry [M6] cluster

2.1.1 The Genesis of the Cluster Series

During the analysis of clusters, a K(n) parameter was introduced(Kiremire, 2017a-f, 2018a-d). The parameter can be transformed into a numerical value of electrons given by VE=18n-2K for transition metal clusters or VE=8n-2K for main group elements. Let us consider an example of K(n)=11(6) parameter. The corresponding VE=18n-2K=18[6]-2[11]=86 for transition metals and VE=8[6]-2[11]=26 for main group elements. The difference between transition metal and main group clusters is given by ∆VE=[(18n-2K)-(8n-2K)]=18n-2K-8n+2K=18n-8n=10n. In this case, n=6 and hence ∆VE= 10[6]=60 which is the same as 86-26=60. What triggered the investigation into the genesis of the cluster series was a simple question. What happens to VE or K when (n) = 0? This relationship is expressed in Scheme 1.



Scheme 1. Relationship between VE, n and K

The chemical clusters follow the K(N) sequences very well. In this regard, let us examine the changes in the K(n) parameter when there is a decrease in (K) by 3 units and (n) by 1 unit, that is, ∆K(n) = -3(-1) or simply a change by 3(1). A good starting point is K(n)=11(6) since this represents an ideal symmetry of an octahedron. Thus, the following K(n) values can readily be generated: 11(6)→8(5) →5(4) →2(3) →-1(2) →-4(1) →-7(0); ∆[K(N)]= =3(1) corresponds to ∆VE=18N-2K=18[1]-2[3]=12. This means there is a corresponding decrease in cluster valence electron content of 12 at every step. When the K(n) variation of 2(1) decrease is performed starting with K(n)= 11(6), we get the following series: 11(6)→9(5) →7(4) →5(3) →3(2) →1(1) →-1(0). In this case as well, ∆[K(N)]=2(1)which corresponds to ∆VE=18N-2K≡18[1]-2[2]=14. Thus, there is a decrease of 14 electrons at every step. What does K(n)= -7(0) mean in terms of cluster valence electrons content? This leads us to apply the simple natural equation VE=18n-2K=18[0]-2[-7]=14. Performing a similar calculation for K(n)= -1(0) we get VE=18n-2K=18[0]-2[-1]= 2. The numerical value [14] is extremely important as it represents the starting point of the [M6] clan series. The [M6] symbol represents a fragment which belongs to the closo family of clusters that follow the series S =4n+2. The figure [14] is also a constant of an ARITHMETIC PROGRESSION whose COMMON DIFFERENCE is equal to12. Likewise, the numerical value of [2] is a constant of an arithmetic progression whose common difference = 14. The generation of K(n) series associated with |∆[K(N)] |= 3(1) and |∆[K(N)] |=2(1) are given in Table1. Also the conversion of K(n) into VE values is illustrated in Scheme 2.

Table 1. Selected K(N) values for [M6] to [M0] clan series

[M6]	[M5]	[M4]	[M3]	[M2]	[M1]	[M0]
11(6)	9(5)	7(4)	5(3)	3(2)	1(1)	-1(0)
8(5)	6(4)	4(3)	2(2)	0(1)	-2(0)	
5(4)	3(3)	1(2)	-1(1)	-3(0)		
2(3)	0(2)	-2(1)	-4(0)			
-1(2)	-3(1)	-5(0)				
-4(1)	-6(0)					
-7(0)						

K(n)=11(6); VE=18n-2K=18(6)-2(11)=86
K(n)=9(5); VE=18n-2K= 18(5)-2(9)=72
K(n)=7(4); VE=18n-2K=18(4)-2(7)=58
K(n)=5(3); VE=18n-2K=18(3)-2(5)=44
K(n)=3(2); VE=18n-2K=18(2)-2(3)=30
K(n)=1(1); VE=18n-2K=18(1)-2(1)=16
K(n)=-1(0); VE=18n-2K=18(0)-2(-1)=2

Scheme2. Converting K(n) into cluster valence electrons VE

Scheme 2. Transforming K(N) into equivalent cluster valence electronsSince we have followed the changes in the K(N) parameter Let us now consider the variation of cluster valence electrons (VE) and the corresponding skeletal number(n) both vertically and horizontally. In this case we can focus on the change of VE(n) parameter with the decrease by Δ[K(N)] =3(1). This means the downward decrease of 12. That is, the cluster valence electrons will decrease step-wise by 12 units. This is a fundamental principle on which the 12N series is based. If we consider the horizontal movement of the series then ΔK(N)=2(1) is utilized. Hence, the change Δ(VE)=18N-2K=18(1)-2(2)=18-4=14. If we define a focal point as VE(n)=86[6] and decrease vertically by VE(n)= 12(1), we get the series: VE(n)=86(6)→74(5) →62(4) →50(3) →38(2) →26(1) →14(0) with a corresponding change in ΔVE=12 →this belongs to the 12N SERIES, S=12n+14**.** The numerical constant at the end in this case 14 represents the additional electrons of the baseline when there is no skeletal element (n= 0) involved. Let us now consider the horizontal movement starting with the same point, 86(6) with a decrease of 14(1) step by step, we get: VE(n) series: 86(6) →72(5) →58(4) →44(3) →30(2) →16(1) →2(0) and ΔVE=14 → this forms the basis of the 14N SERIES, S=14n+2. Like the 12N series, the numerical number 2 represents the additional electrons which are associated with n=0. Selected representatives of the 14N series and the 12N series are shown in Table2. The series can be expressed as S=12n+q' and S= 14n+q where q' and q are numerical values obtained when n=0 in the K(n) and VE(n) variations. In the Tables 1and 2, S= 14n+q series form the rows (families) and the S=12n+q series form the columns (clans). The Rudolph concept of correlation of borane clusters (Rudolph, 1976) corresponds to the clan categorization approach of clusters. In order to examine more VE(n=0) values, that is, q' and q capping values, Table 2 was extended to produce Table s 3, 4 and 5. The VE(n) values in Table 2 can also be expressed in the form of Cartesian coordinates indicated in Figure 2. The proposed assignment of clan and family cluster series is illustrated in Figure 3 and relationships between some of the cluster equations developed during the study of cluster series are shown in Scheme 3.

Table 2. The Genesis of cluster valence electrons VE0 for selected [M6] to [M0] clan series

CLANS [Columns]	[Mx]	[M6]	[M5]	[M4]	[M3]	[M2]	[M1]	[M0]		VE=	
	VE(n)	86(6)	72(5)	58(4)	44(3)	30(2)	16(1)	**2(0)**		14n+2	
	VE(n)	74(5)	60(4)	46(3)	32(2)	18(1)	**4(0)**			14n+4	
	VE(n)	62(4)	48(3)	34(2)	20(1)	**6(0)**				14n+6	
	VE(n)	50(3)	36(2)	22(1)	**8(0)**					14n+8	
	VE(n)	38(2)	24(1)	**10(0)**						14n+10	
	VE(n)	26(1)	**12(0)**							14n+12	
	VE(n)	**14(0)**								14n+14	
	VE=	**12n+14**	**12n+12**	**12n+10**	**12n+8**	**12n+6**	**12n+4**	**12n+2**			
									FAMILIES[Rows]		

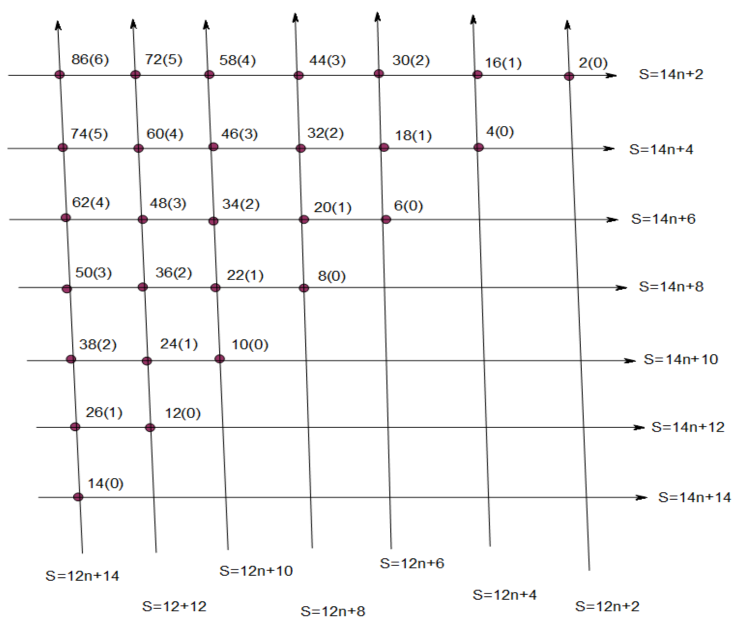


Figure 2. A sketch of VE(n) map of selected cluster clan series

Table 3. Upward Extension of Table 2

N	VE													S=14n+q	C^n
23	**290**	276	262	248	234	220	206	192	178	164	150	136	122	**14n-32**	C^{17}
22	**278**	264	250	236	222	208	194	180	166	152	138	124	110	**14n-30**	C^{16}
21	**266**	252	238	224	210	196	182	168	154	140	126	112	98	**14n-28**	C^{15}
20	**254**	240	226	212	198	184	170	156	142	128	114	100	86	**14n-26**	C^{14}
19	**242**	228	214	200	186	172	158	144	130	116	102	88	74	**14n-24**	C^{13}
18	**230**	216	202	188	174	160	146	132	118	104	90	76	62	**14n-22**	C^{12}
17	**218**	204	190	176	162	148	134	120	106	92	78	64	50	**14n-20**	C^{11}
16	**206**	192	178	164	150	136	122	108	94	80	66	52	38	**14n-18**	C^{10}
15	**194**	180	166	152	138	124	110	96	82	68	54	40	26	**14n-16**	C^{9}
14	**182**	168	154	140	126	112	98	84	70	56	42	28	14	**14n-14**	C^{8}
13	**170**	156	142	128	114	100	86	72	58	44	30	16	2	**14n-12**	C^{7}
12	**158**	144	130	116	102	88	74	60	46	32	18	4	**-10(0)**	**14n-10**	C^{6}
11	**146**	132	118	104	90	76	62	48	34	20	6	**-8(0)**	**-22**	**14n-8**	C^{5}
10	**134**	120	106	92	78	64	50	36	22	8	**-6(0)**	**-20**	**-34**	**14n-6**	C^{4}
9	**122**	108	94	80	66	52	38	24	10	**-4(0)**	**-18**	**--32**	**--46**	**14n-4**	C^{3}
8	**110**	96	82	68	54	40	26	12	**-2(0)**	**-16**	**-30**	**-44**	**-58**	**14n-2**	C^{2}
7	**98**	84	70	56	42	28	14	**0(0)**	**-14**	**-28**	**-32**	**-46**	**-60**	**14n+0**	C^{1}
6	**86**	72	58	44	30	16	**2(0)**	**-12**	**-26**	**-40**	**-54**	**-68**	**--72**	**14n+2**	C^{0}
	[M6]	[M5]	[M4]	[M3]	[M2]	[M1]	**[M0]**	M-1	M-2	M-3	M-4	M-5	M-6		
12n+q	**q=14**	12	10	8	6	4	**2**	0	-2	-4	-6	-8	-10		

Table 4. Further extension of Table 2

218	**204**	**190**	**176**	**162**	**148**	**134**	**120**	**106**	**92**	**78**
206	**192**	**178**	**164**	**150**	**136**	**122**	**108**	**94**	**80**	**66**
194	**180**	**166**	**152**	**138**	**124**	**110**	**96**	**82**	**68**	**54**
182	**168**	**154**	**140**	**126**	**112**	**98**	**84**	**70**	**56**	**42**
170	**156**	**142**	**128**	**114**	**100**	**86**	**72**	**58**	**44**	**30**
158	**144**	**130**	**116**	**102**	**88**	**74**	**60**	**46**	**32**	**18**
146	**132**	**118**	**104**	**90**	**76**	**62**	**48**	**34**	**20**	**6**
134	**120**	**106**	**92**	**78**	**64**	**50**	**36**	**22**	**8**	**-6**
122	**108**	**94**	**80**	**66**	**52**	**38**	**24**	**10**	**-4**	**-18**
110	**96**	**82**	**68**	**54**	**40**	**26**	**12**	**-2**	**-16**	**-30**
98	**84**	**70**	**56**	**42**	**28**	**14**	**0**	**-14**	**-28**	**4n-28**
86	**72**	**58**	**44**	**30**	**16**	**2**	**-12**	**-26**	**4n-26**	
74	**60**	**46**	**32**	**18**	**4**	**-10**	**-24**	**4n-24**		
62	**48**	**34**	**20**	**6**	**-8**	**-22**	**4n-22**			
50	**36**	**22**	**8**	**-6**	**-20**	**4n-20**				
38	**24**	**10**	**-4**	**-18**	**4n-18**					
26	**12**	**-2**	**-16**	**4n-16**						
14	**0**	**-14**	**4n-14**							
2	**-12**	**4n-12**								
-10	**4n-10**									

Table 5. **Additional further extension of Table 2**

64	50	36	22	8
52	38	24	10	-4
40	26	12	-2	-16
28	14	0	-14	-28
16	2	-12	-26	**-40**
4	-10	-24	**-38**	**4n-38**
-8	-22	**-36**	**4n-36**	
-20	**-34**	**4n-34**		
-32	**4n-32**			

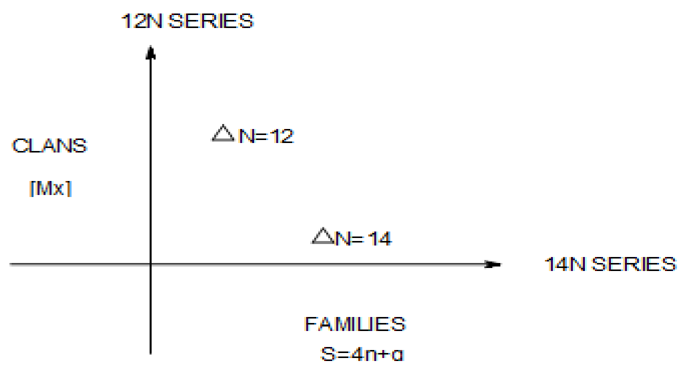
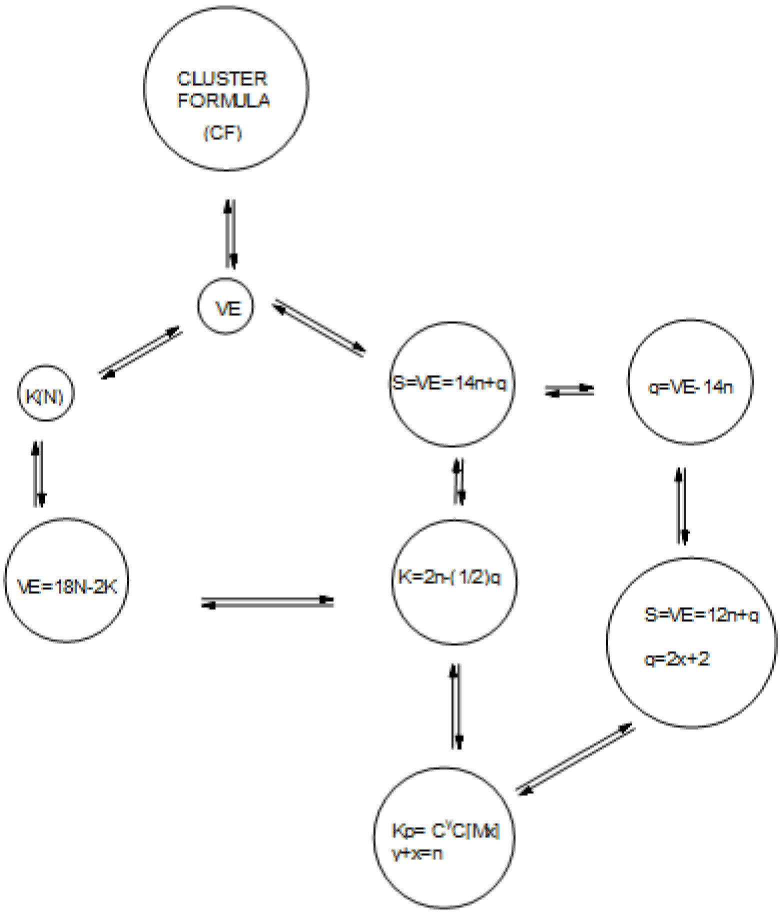


Figure 3. Defining clans and gamilies of clusters



Scheme 3. Relationships of important cluster equations

2.1.2 The Capping Theory Concept as Derived from the Genesis of the 4N Series

The series general formula S=4n+q for categorizing clusters that was empirically derived(Kiremire, 2016c) can be utilized to determine cluster valence electrons, VE. The cluster valence electrons, VE = 4n+q for the main group clusters and VE =14n+q for transition metal clusters. As can be seen from array of cluster valence electrons in Tables 2-5, the series formula is a consequence of the natural sequence of the cluster valence electrons. Thus, the 14n and q components of the series formula S=14n+q occur naturally from the arrays of the cluster valence electrons. For ease of application, the formula is adjusted to the simpler one S=4n+q for usage in the categorization of clusters of transition metals and main group elements. Both the cluster valence electrons and formulas can readily be derived from the capping principles of clusters. Furthermore, the relationship between VE and q becomes clearer. As can readily be deduced from Table 2 horizontally or vertically, the cluster valence electrons (VE) can be calculated from the relationship VE= q+14n = q'+12n. For instance, VE=2+6[14]=86 and VE=14+6[12]=86. In terms of deducing the type of cluster series it has been found easier to apply q derived horizontally rather than the q' derived vertically. The q' becomes useful in sketching the capping diagrams of clusters as will be illustrated by examples in this paper. We can express the above concepts as follows:

VE = q+ VE1+VE2+VE3+……+VEn; and since VE1= VE2= VE3=….. VEn = 14, then VE= q+14n = S(horizontal series)

VE=q'+ VE1+VE2+VE3+……+VEn; and since VE1= VE2= VE3=….. VEn = 12, then VE= q'+12n = S(vertical series)

A cluster formula can also be derived by transforming the cluster valence electrons into chemical fragments using the relevant cluster series. Let us illustrate this using $Rh_6(CO)_{16}$ as an example;

VE=86, n=6; 86=6[14]+2=14n+2(n=6), 86=6[12]+14=12n+14(n=6).

VE= 14n+2; F= $[RhH(CO)_2][6]+CO = Rh_6H_6(CO)_{12}+CO = Rh_6(CO)_3(CO)_{12}+CO = Rh_6(CO)_{16}$. In this case, the 2 in the series is replaced with a two electron donor CO.

Using VE=12n+14; we get, F=$[RhH(CO)](6)+7CO = Rh_6H_6(CO)_6+7CO = Rh_6(CO)_3(CO)_6+7CO = Rh_6(CO)_{16}$. The [14] numerical has been replaced by 7CO which donate a total of 14 electrons.

The above examples and formulas demonstrate some of the ways the clusters are interlinked via series. The above concepts provide us with a hint of how to convert VE(n) into either the 14N or 12N series. For instance, VE(n)=86(6); VE=14n+q,hence q=VE-14n=86-14[6]=2. This results into S=14n+2. For the 12N series, q'=VE-12n = 86-12[6]=14. Hence, S=12n+14.

2.2 Types of Capping Phenomena

A given VE(n) parameter is at the intersection of the horizontal (S=14n+q) and vertical(S=12+q') series. There is also diagonal series that could be considered. However, it been found easier to analyze the capping series using the vertical ones, S=12n+q' but categorization and cluster valence determination to use the horizontal series formula S=14n+q or simply, S=4n+q.

Using the 12N series approach to differentiate the types of capping phenomena

The capping formula Kp= $C^yC[Mx]$(y+x=n) developed earlier(Kiremire,2015b) is quite useful in guiding us to broadly differentiate the different types of capping phenomena. In general, we can classify the capping clusters into 3 broad categories.

2.2.1 (A): Kp= $C^yC[Mx]$, y≥0 and x≥1

The symbol,[Mx] represents nucleus centered clusters. Such clusters have one or more skeletal elements in the nucleus. The nucleus on its own belongs to the CLOSO family which follows the S=4n+2 series. Ideally, the nuclei behave like closo borane fragments$[B_nH_n]^{2-}$. Examples include [M1] centered with one skeletal element in the nucleus; the corresponding baseline cluster valence electrons are given by VE0= 2n+2=2[1]+2=4; [M2] with 2 skeletal elements in the nucleus and the corresponding VE0=2n+2=2[2]+2=6,[M5] with 5 skeletal elements in the nucleus and corresponding VE0=2n+2=2[5]+2=12 and [M6] with 6 skeletal elements in the nucleus .and corresponding VE0=2n+2=2[6]+2=14. The capping trees of such clusters with selected examples are given in Figures 4-7. The example of the cluster tree in Figure 8 of main group elements is added for comparison with the corresponding ones from transition elements.

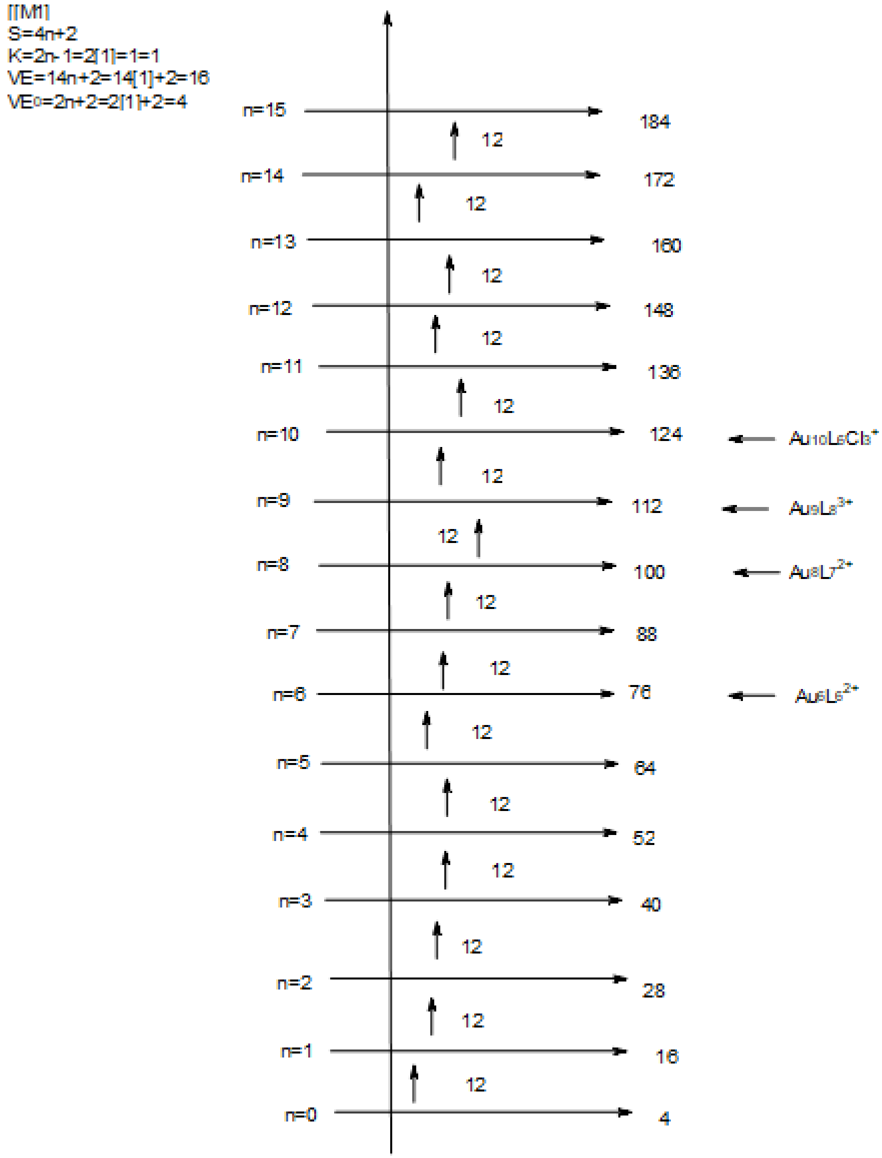


Figure 4. **A sketch** of the capping tree of [M1] cluster clans series

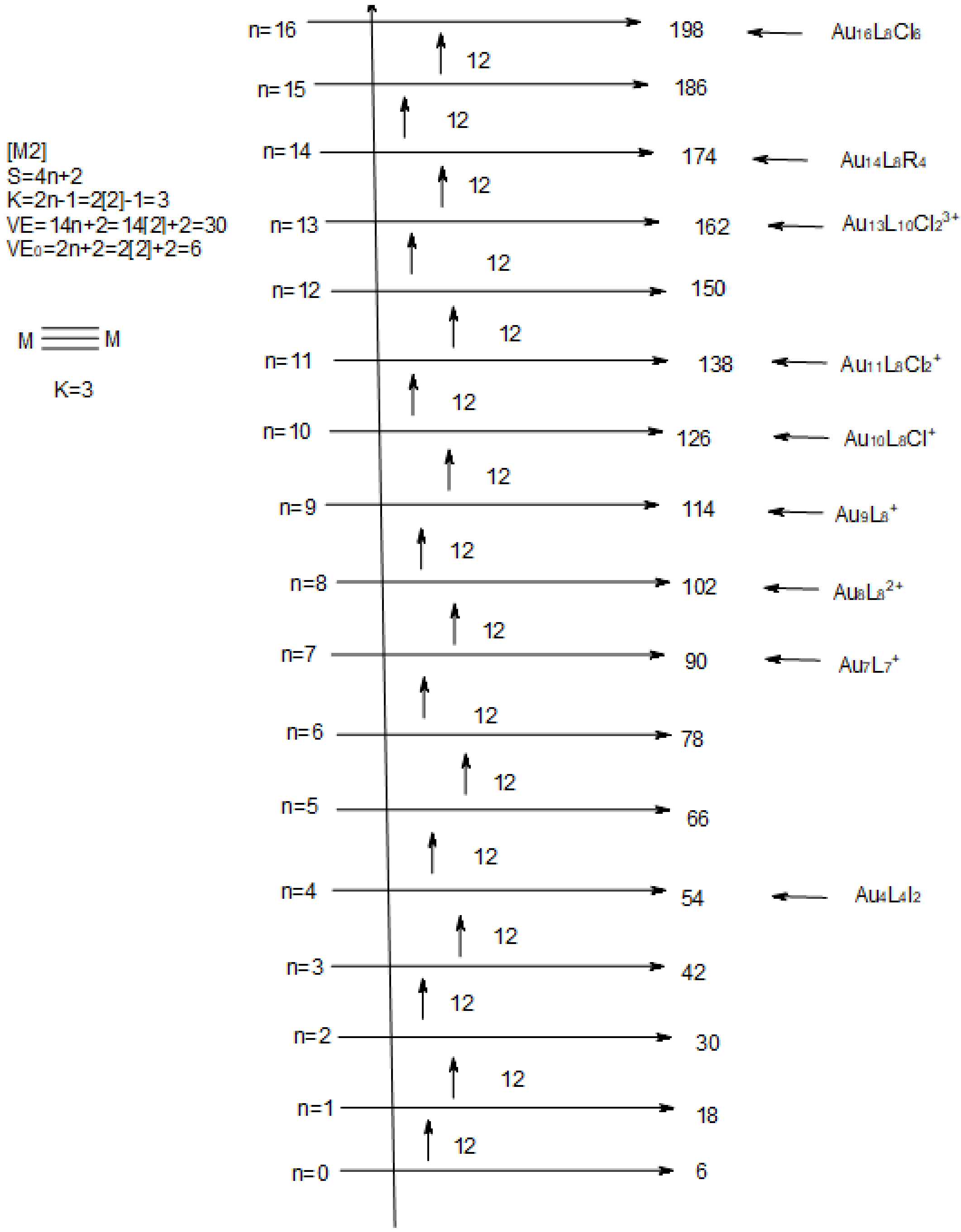


Figure 5. **A sketch** of a capping tree of [M2] cluster clan series

2.2.1.1 Correlating a Cluster Formula to a Clan Tree

Take the [M2] clan series as an illustration

The cluster formulas are interlinked with their respective tree. Let us illustrate this point with the examples of clusters attached to the [M2] clan tree.

1. $F=Au_4L_4I_2$:VF=4[11]+4[2]+2[1]= 54,n=4

   VE0=2n+2(n=2) =2[2]+2=6

   VE=VE0+12n

   VE4=6+12[4]=54

   F=F0+nF

   $F=6R+4[AuR]=Au_4R_4+6R=Au_4R_{10}$

   $F=Au_4L_4I_2=Au_4R_8R_2=Au_4R_{10}$

   R= 1 electron donor, L= 2 electron donor=2R.

2. $F=Au_8L_8^{2+}$:n=8, VE0=6, VE=VE0+12n=6+12[8]=102,VF=8[11]+8[2]-2=102

   $F=F0+nF=6R+8[AuR]=Au_8R_{14}$; $F= Au_8L_8^{2+}=Au_8R_{16}-2R=Au_8R_{14}$.

3. $F=Au_{13}L_{10}Cl_2^{3+}$:n=13, VE0=6,VE=VE0+12n=6+12[13]=162, VF=13[11]+10[2]+2[1]-3=162

   $F=F0+nF=6R+13[AuR]=Au_{13}R_{13}+6R=Au_{13}R_{19}$; $F= Au_{13}L_{10}Cl_2^{3+}=Au_{13}R_{20}R_2-3R=Au_{13}R_{19}$.

4. $F= Au_{16}L_8Cl_6$: VF=16[11]+8[2]+6[1]=198

   VE=VE0+12n

   VE16=6+12[16]=198

   F=F0+nF

   $F= 6R+16[AuR]=Au_{16}R_{22}$

   $F= Au_{16}L_8Cl_6=Au_{16}R_{16}R_6=Au_{16}R_{22}$

   Other examples can be tested in the same way.

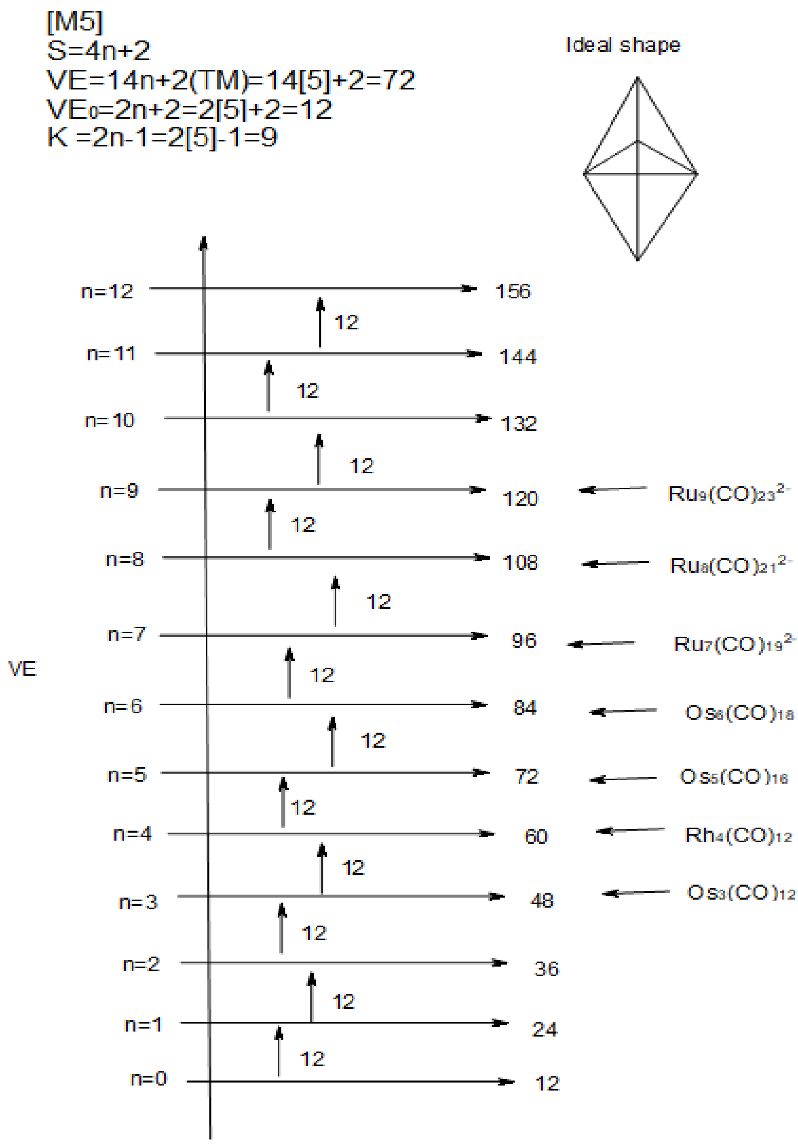


Figure 6. A sketch of the capping tree of [M5] cluster clan series

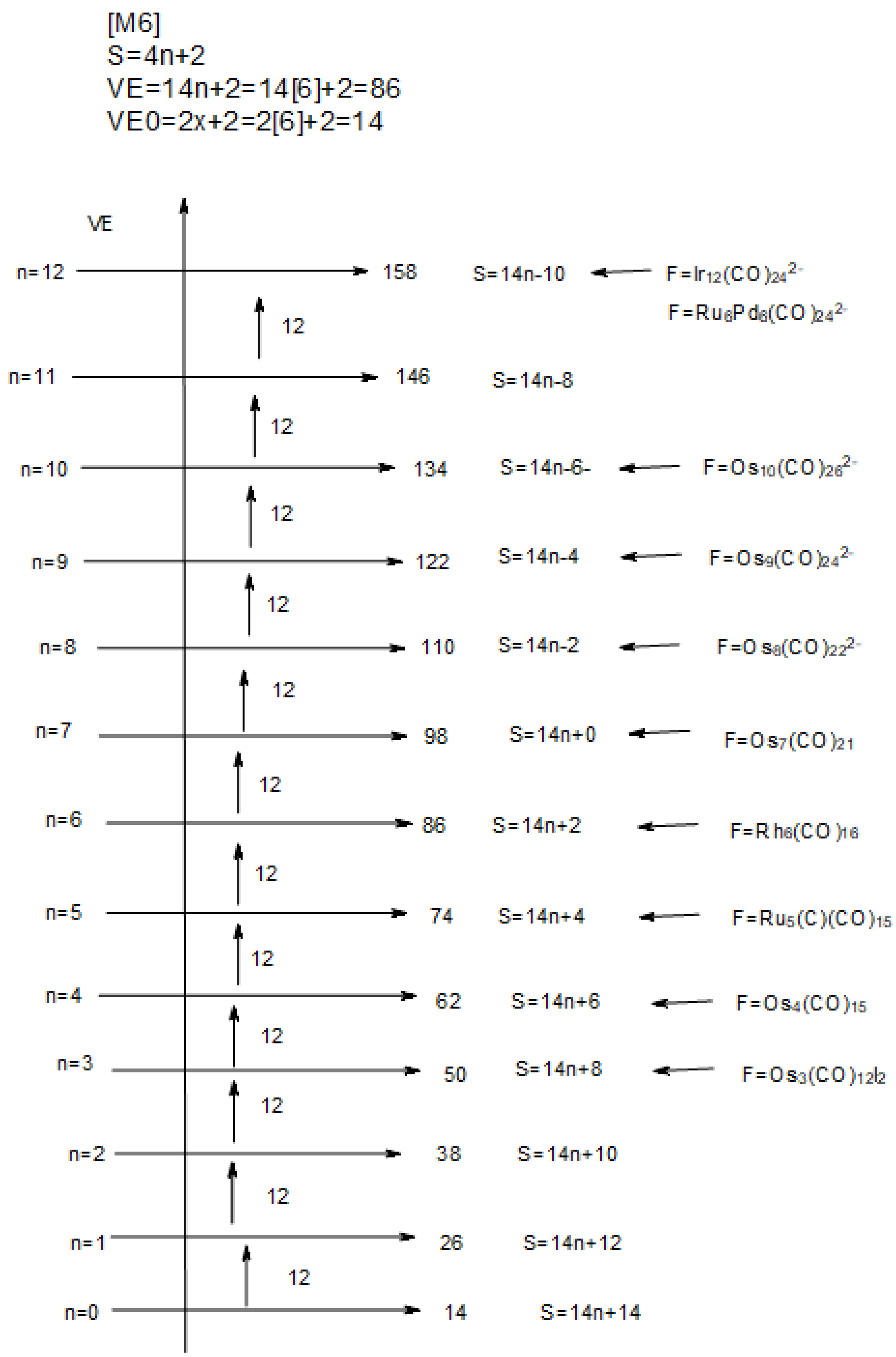


Figure 7. Sketch of the capping tree for the [M6] cluster clan series for transition metal elements

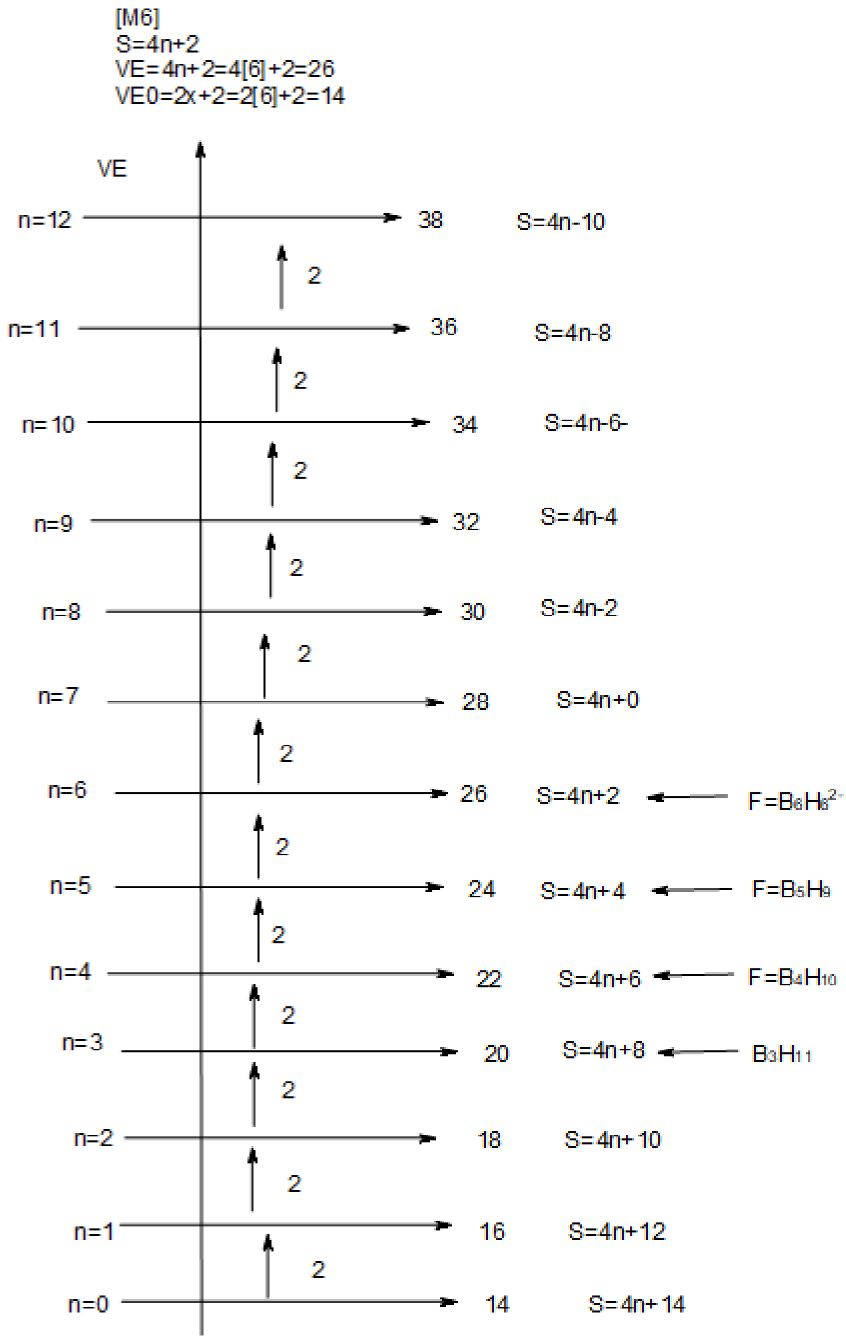


Figure 8. A capping tree for [M6] clan series for main group elements

2.2.2 (B) K= $C^yC[Mx]$, y≥0 and x=0;VEO=2n+2=2[0]+2=2

These capping clusters have 2 electrons in the nucleus without a skeletal element. These include $Os_{20}(CO)_{40}^{2-}$, VE(n)=242(20); $Au_{20}L_{10}Cl_4^{2+}$, 242(20); $Au_{22}L_{12}$, 266(22) and $Au_{24}L_{10}R_5X_2^{+}$, 290(24). The selected VE(n) series are shown in Table 5**.These are categorized as [M0] clan cluster series. The positions of these cited examples are highlighted in the table.

Table 6. Selected capping cluster valence electrons of [M0] series

		C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}	C^{13}
VE	2	14	26	38	50	62	74	86	98	110	122	134	146	158
n	0	1	2	3	4	5	6	7	8	9	10	11	12	13
	C^{14}	C^{15}	C^{16}	C^{17}	C^{18}	C^{19}	C^{20}	C^{21}	C^{22}	C^{23}	C^{24}	C^{25}	C^{26}	C^{27}
VE	170	182	194	206	218	230	**242**	254	**266**	278	**290**	302	314	326
n	14	15	16	17	18	19	**20**	21	**22**	23	**24**	25	26	27

2.2.3 Type (C): K= $C^yC[Mx]$, y≥0 and x≤0; Existence of Black-holes in the Cluster Nucleus

Let us consider the following examples as illustrations. These clusters have negative nuclearity index, x= -1,-2,-3,-4 and so on. There is a significant difference say between [M2] and [M-2]. In the case of [M2], the cluster has 2 capping skeletal elements each carrying 12 cluster electrons whereas in the case of [M-2], the nucleus has two empty sets of 12 electrons capping in the cluster nucleus, that is, a nucleus without any skeletal elements. A nucleus of negative nuclearity index has been referred to as a black-hole(Kiremire, 2018d) and in this example of [M-2], the negative 2 are also regarded as mini-holes each containing 12 capping electrons. Negative nuclearity index could be regarded as a characteristic of metallic skeletal elements. This concept is further illustrated by the examples in Figures 9-13 for clusters with black-holes and Figures 14-19 for naked skeletal elements for comparison.

$Pd_{54}(CO)_{40}L_{14}$:VE=54[10]+40[2]+14[2]=648
q=648-14[54]= -108
S=4n-108
K=2n+54
Kp=$C^{55}C$[M-1]
Kp'=D^1+C^{*54}
This can be translated as a capping black-hole in the cluster nucleus containing 12 electrons surrounded by 54 capping skeletal elements.
VE0=2n+2(n=for the nucleus)=2[-1]+2=0
VEC=14n+2(n=for the nucleus)=14[-1]+2= -12
With this information, we can sketch a cluster capping diagram.

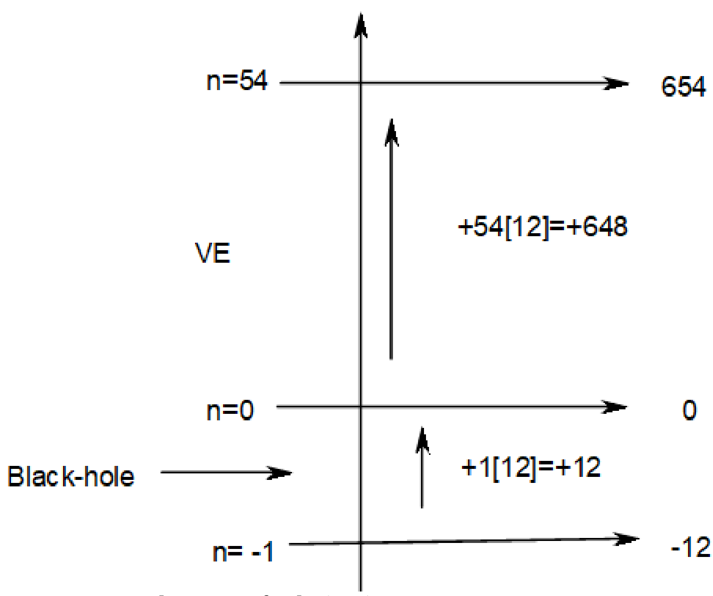


Figure 9. A capping diagram of $Pd_{54}(CO)_{40}L_{14}$

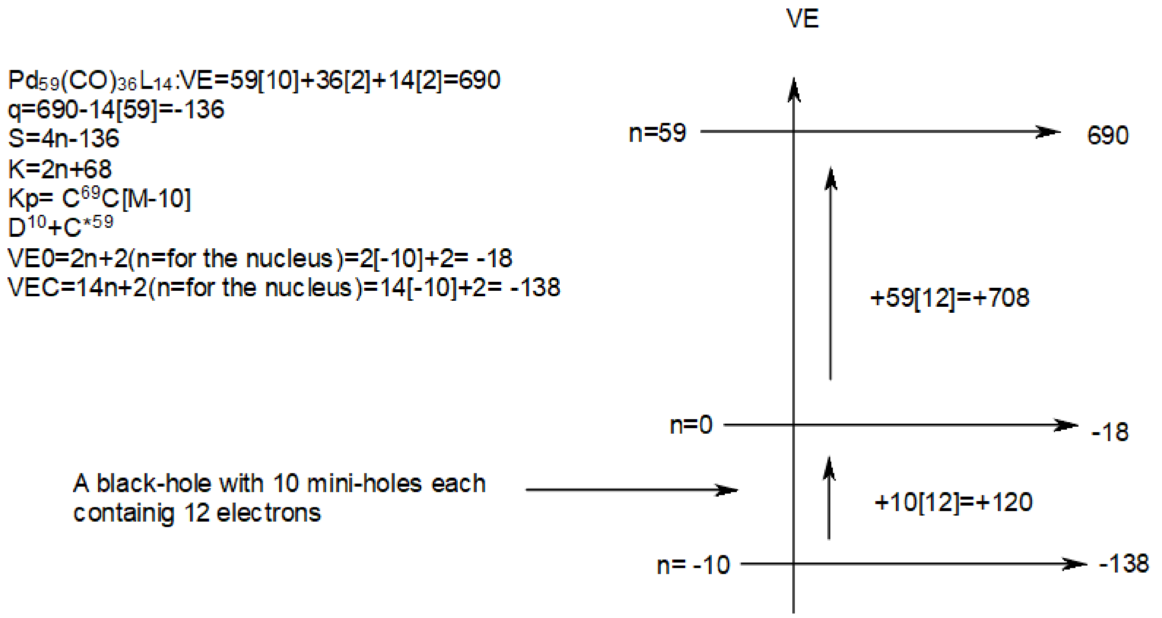


Figure 10. A capping diagram of $Pd_{59}CO)_{36}L_{14}$

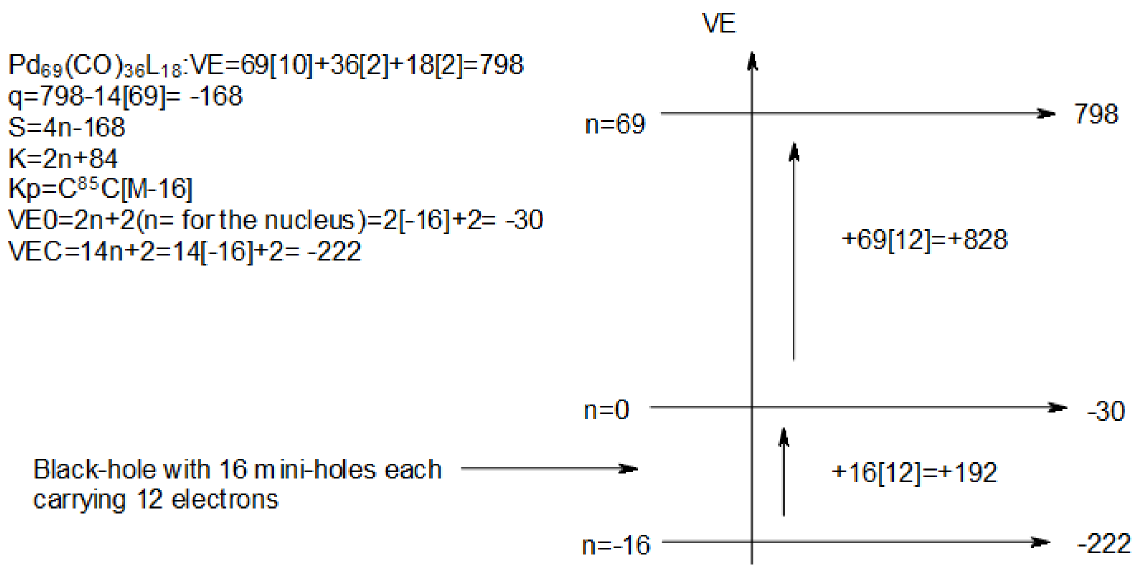


Figure 11. A capping diagram of $Pd_{69}CO)_{36}L_{18}$

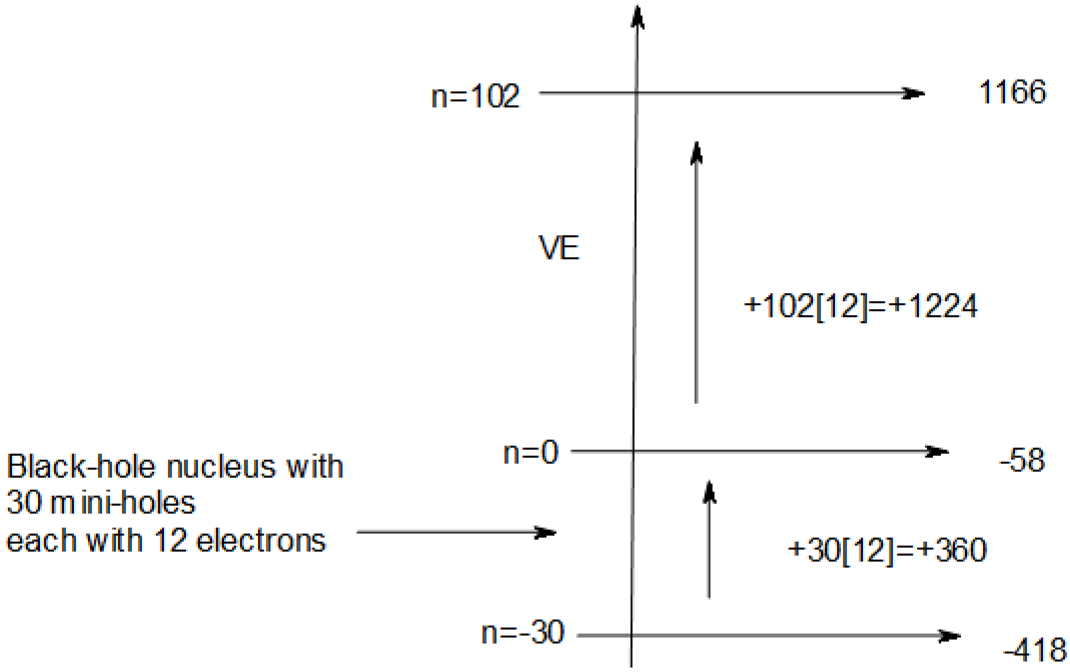


Figure 12. A capping diagram of $Au_{102}R_{44}$

F= $Pd_{165}(CO)_{60}L_{30}$:VE=165[10]+60[2]+30[2]=1830,n=165
VE(n)=1830(165)
1830-165[14]= -480
S=14n-480
K=2n+240
Kp=C^{241}C[M-76]
Kp=D^{76}+C^{*165}
VE0=2n+2=2[-76]+2= -150
VEC=14n+2= 14[-76]+2=-1062

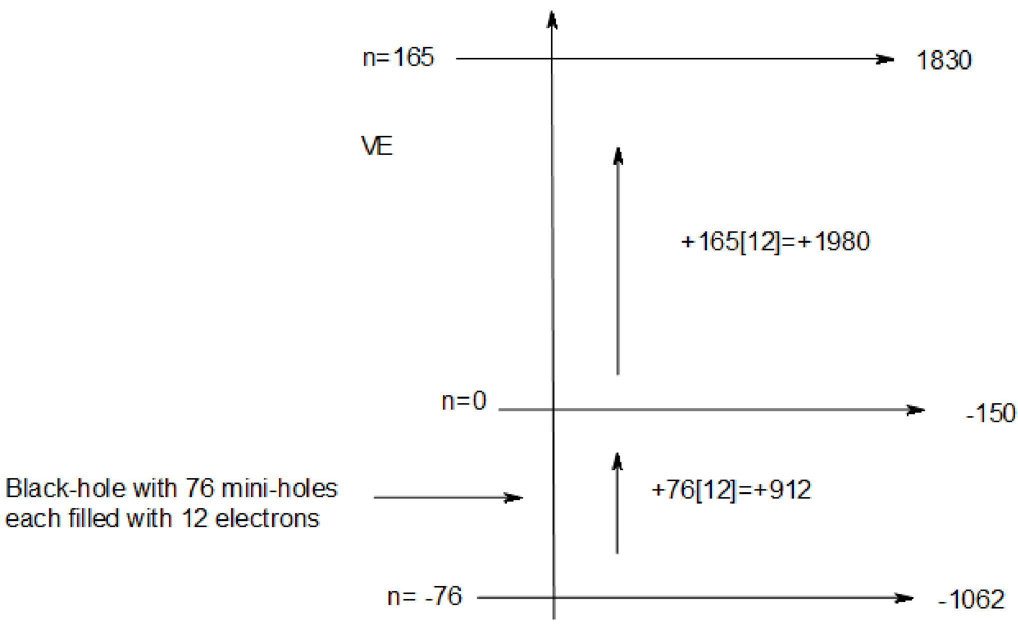


Figure 11. A capping diagram of $Pd_{165}CO)_{60}L_{30}$

2.3 Metallic and Non-Metallic Elements

It has been found that the capping method which has been applied to clusters can equally well be applied to metallic and non-metallic elements from main group and transition elements. A transition element has a set of valence electrons (VE) associated with it and since it is one, then clearly n=1. Hence, it obeys the 14N series. Hence, q=VE-14n formula can readily be applied to them. Let us consider Ti (VE=4, n=1), hence q=4-14[1]= -10 and S=4n-10, K=2n+5, $Kp=C^6C[M-5]$, $Kp'=D^5+C^{*1}$. This symbol means, Ti possesses 5 sets of 12 capping electrons in its black-hole nucleus and one capping skeletal element. The capping phenomenon commences at VEC=14n+2 = 14[-5]+2 = -68. This is a low level of deficit -68 e and when the 5 sets of capping dozen electrons are added, there is a balance of deficit of -8e. However, the black-hole is now filled. According to the 12N capping principle, when the only first skeletal fragment of 12 electrons is added on top the net becomes 4 which now becomes the observed valence electrons of $Ti[Ar]4s^23d^2$. Other transition metal skeletal elements may be rationalized in the same hypothetical manner. As can be seen from Tables 6 and 7, the transition elements are characterized by valence electron deficit (VE0<0) on capping giving rise to a decreased value of the valence electrons (VE)than the capping set of 12 electrons that were added(Table 6) while in the case of the main group elements the valence electrons VE obtained after the two capping electrons are more than VE0(the number of valence electrons before the capping skeletal element has been added). Thus, the capping principle can be used as a simple qualitative guide to distinguish between metals and non-metals. The metallic elements have VE0<0, non-metallic VE0>0 and VE0=0 may be regarded as a borderline case. The borderline transition metal elements are Zn, Cd and Hg while the corresponding main group elements are Be, Mg, Ca, Sr, Ba and Ra The VE0<0 for group 1 elements, Li, Na, K, Rb, Cs, Fr implying that they may strictly be regarded as being metallic in character.

Table 7. The capping data of naked transition metals

ELEMENT	K VALUE	$K=C^yC[Mx]$; y+x=n, n=1	D VALUE Mini-holes in the nucleus	CAPPING ELECTRONS	VE0=2x+2 ELECTRON DEFICIT	VE=VE0+12
Sc, Y, Lu	7.5	$C^{6.5}C[M-5.5]$	5.5	66	-9	3
Ti, Zr, Hf	7	$C^6C[M-5]$	5	60	-8	4
V, Nb, Ta	6.5	$C^{5.5}C[M-4.5]$	4.5	54	-7	5
Cr,Mo, W	6	$C^5C[M-4]$	4	48	-6	6
Mn, Tc, Re	5.5	$C^{4.5}C[M-3.5]$	3.5	42	-5	7
Fe, Ru, Os	5	$C^4C[M-3]$	3	36	-4	8
Co, Rh,Ir	4.5	$C^{3.5}C[M-2.5]$	2.5	30	-3	9
Ni, Pd, Pt	4	$C^3C[M-2]$	2	24	-2	10
Cu, Ag, Au	3.5	$C^{2.5}C[M-1.5]$	1.5	18	-1	11
Zn, Cd, Hg	3	$C^2C[M-1]$	1	12	0	12

Table 8. The capping data for the Main group Elements

T8				
MAIN GROUP ELEMENTS	K VALUE	$K=C^yC[Mx]$	VE0=2x+2	VE=VE0+2
Li, Na, K, Rb, Cs, Fr	3.5	$C^{2.5}C[M-1.5]$	-1 (deficit)	1
Be, Mg, Ca, Sr, Ba,Ra	3	$C^2C[M-1]$	0	2
			ELECTRON SURPLUS	
B, Al, Ga, In, Tl	2.5	$C^{1.5}C[M-0.5]$	1	3
C, Si, Ge, Sn,Pb	2	$C^1C[M0]$	2	4
N, P, As, Sb, Bi	1.5	$C^{0.5}C[M0.5]$	3	5
O, S, Se, Te, Po	1	$C^0C[M1]$	4	6
F, Cl, Br, I, At	0.5	$C^{-0.5}C[M1.5]$	5	7
Ne, Ar, Kr, Xe, Rn	0	$C^{-1}C[M2]$	6	8

Ti, VE=4,n=1
q=VE-14n=4-14[1]=4-14= -10
S=4n+q
S=4n-10
K=2n+5
$Kp=C^6C[MM-5]$
$Kp'=D^5+C^{*1}$
According to the 4N series approach, the capping element has a black-hole nucleus with 5 mini-holes each field with 12 electrons.
VE0=2n+2(n=for nucleus)=2[-5]+2=-8
VEC=14n+2(n=for the nucleus)=14[-5]+2=-68

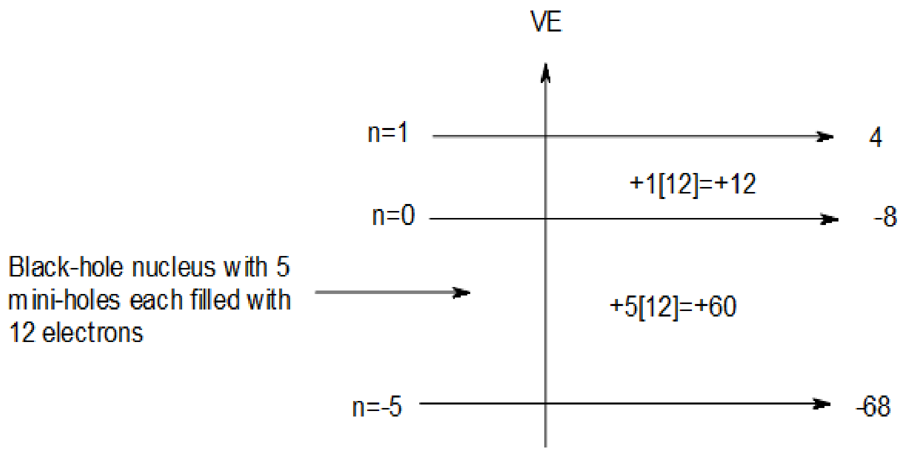


Figure 14. A capping diagram for Ti

The titanium element not only does it possess a black-hole nucleus, it has a deficit of capping electrons which results into a net of 4 valence electrons.

Cr, VE=6, n=1
q=6-14[1]=-8
S=4n-8
K=2n+4
$Kp=C^5C[M-4]$
$Kp'=D^4+C^{*1}$
A black-hole nucleus with 4 mini-holes each field with 12 electrons.
VE0=2n+2=2[-4]+2=-6
VEC=14n+2=14[-4]+2=-54

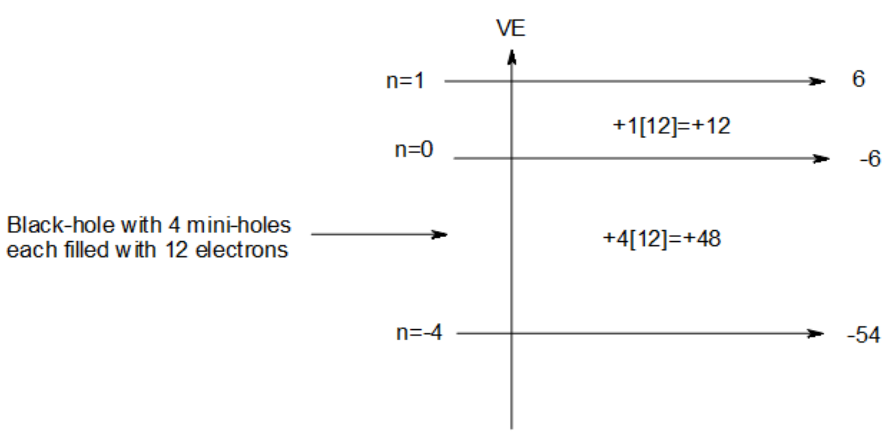


Figure 15. A capping diagram of Cr

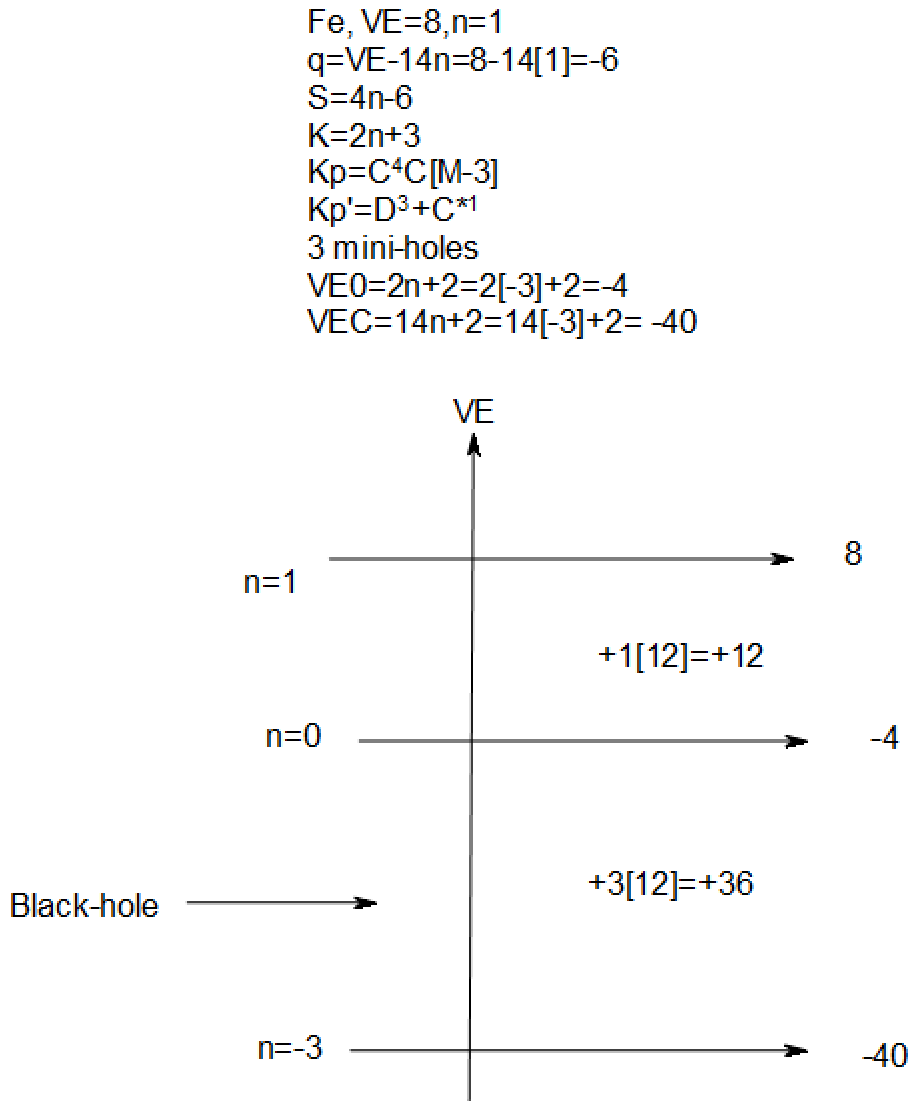


Figure 16. A capping diagram of Fe

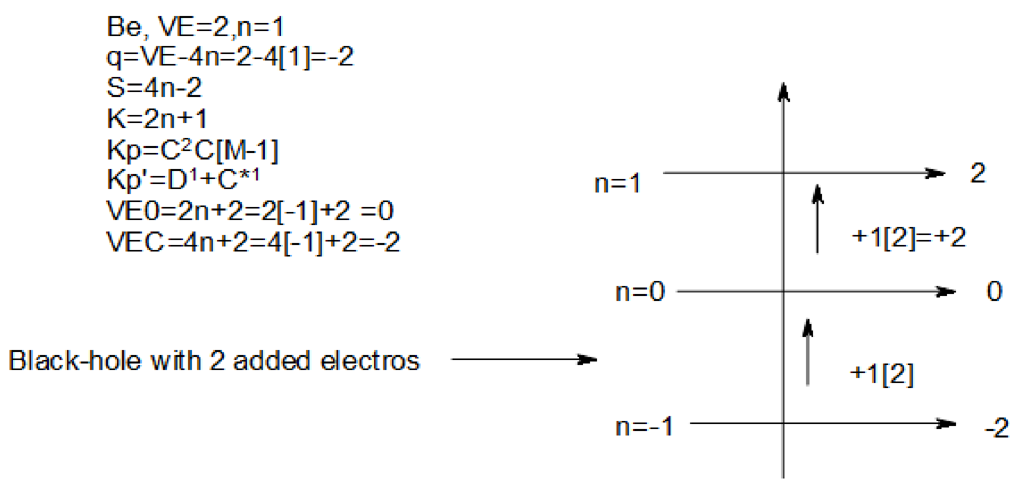


Figure 17. A capping diagram of Be

C, VE=4,n=1
q=VE-4n=4-4[1]=0
S=4n+0
K=2n+0
Kp=C^1C[M0]
VE0=2n+2=2[0]+2=2
VEC=4n+2=4[0]+2=2

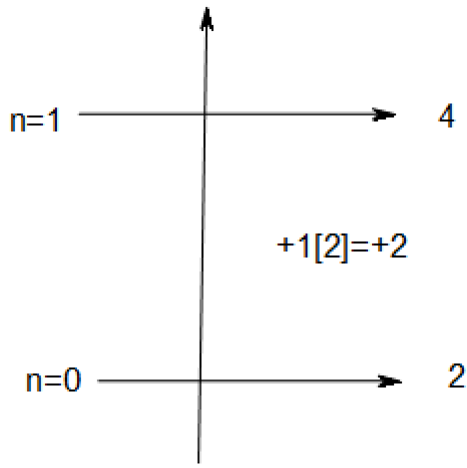


Figure 18. A capping diagram C

O, VE=6,n=1
q=VE-4n=6-4[1]=2
S=4n+2
K=2n-1
Kp=C^0C[M1]
VE0=2n+2=2[1]+2=4
VEC=4n+2=4[1]+2=6

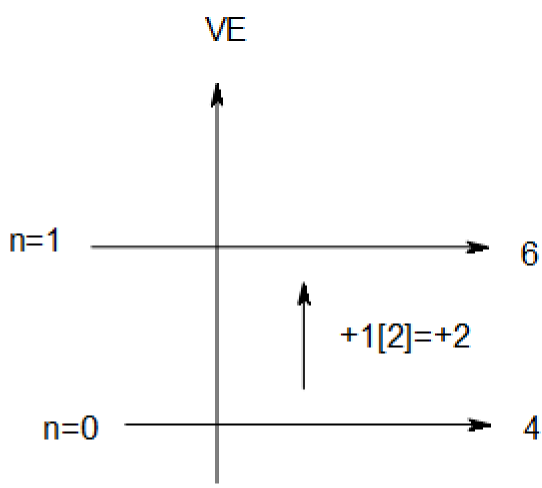


Figure 19. A capping diagram O

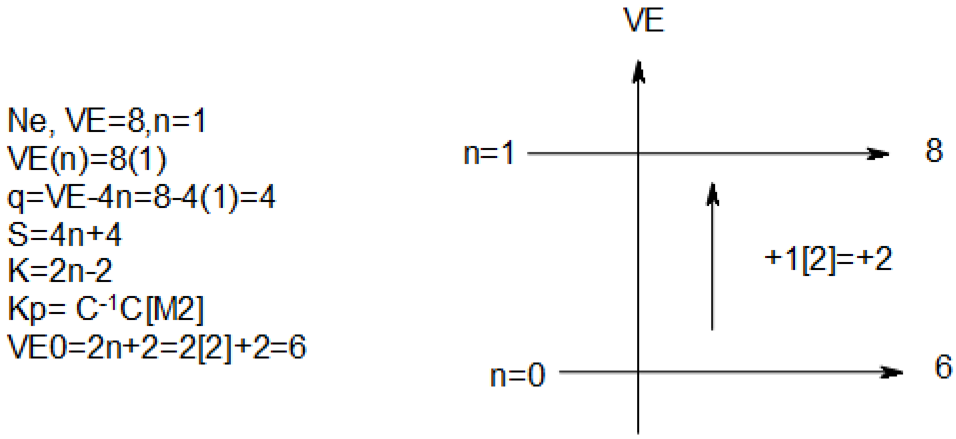


Figure 20. A capping diagram Ne

2.4 Grouping of Skeletal Elements

The analysis of capping clusters using the 4N series method naturally leads to categorizing them into 2 groups. The capping symbol is expressed as Kp= $C^yC[Mx]$where y+x=n, the number of skeletal elements in a cluster. The skeletal elements represented by (y) are the capping ones, normally residing in the OUTER SHELL of the cluster and those represented by(x) are the ones residing in the INNER SHELL, the fragment referred to as the nucleus of the cluster. A collection of more than 20 examples have been worked out to demonstrate the power of the capping formula in grouping the skeletal elements of capping clusters. Even when a cluster is not capped beyond the closo baseline, the formula can indicate to what clan cluster group it belongs.

1. $Sn_{21}Cu_{12}^{12-}$: K=21[2]+12[3.5]-6=78, n=21+12=33

K(n)=78(33)

66-78= -12

S=4n-24

K=2n+12

Kp=$C^{13}C$[M20]

Kp'=$C^{13}+D^{20}$

Kp''=C^1(Sn)+C^{12}(Cu)+D^{20}(Sn)

This cluster may be regarded as a Zintl-type of matryoshka cluster. The capping formula of the 4N series can only separate the skeletal elements of a capping cluster INTO 2 GROUPS . At this level of its qualitative application, it is unable to go deeper into details. The details can only be elucidated by x-ray crystal structural analysis. In this case, the cluster of 13 skeletal elements is found to comprise of Sn at the center of an icosahedral cluster enclosed in another cluster of 20 Sn skeletal elements(Huang, et al, 2014).

The capping formula Kp' = $C^{13}+D^{20}$ represents 2 types of cluster series; namely for the outer shell, C^y = C^{13}: S1 =4n-2(13)=4n-26, K1= 2n+13=2[13]+13=39=3y; the inner shell, [M20]→D^{20}, S2=4n+2, K2=2n-1= 2[20]-1= 39; S=S1+S2=[(4n-26)+(4n+2)]=4n-24; K=K1+K2=39+39=78. Clearly K1=K2. It appears that this unique equivalence relationship of K1=K2 is characteristic of matryoshka clusters.

2. $Os_{10}(CO)_{26}^{2-}$:VE=10[8]+26[2]+2= 134,n=10

VE=14n+q

q=VE-14n =134-14[10]= -6

S=4n-6

K=2n+3=2[10]+3=23

Kp= C^4C[M6]

Since the nucleus also has capping skeletal elements founded upon base-line cluster valence electron, we could introduce another capping symbol (D) for the elements in the nucleus. The cluster is expressed as a tetra-capped octahedron (Hughe & Wade, 2000).

Thus, Kp'=C^4+D^6; D^6 follows S1=4n+2 and C^4 follows S2=4n-2(4)= 4n-8 series and the net S

=S1+S2=[(4n+2)+(4n-8)]=4n-6;K1=2n-1=2[6]-1=11, K2=2n+4=2[4]+4=12; K=K1+K2=11+12=23

Again, the separation of skeletal elements into two groups, 4 in the outer shell and 6 in the inner shell.

The inner cluster,[M6] has an octahedral shape and belongs to closo series S=4n+2 family. The outer elements follows the capping series S=4n-2(4)=4n-8.

3. F=$Ru_6Pd_6(CO)_{24}^{2-}$:The cluster is observed to be a hexa-capped octahedron(Rossi&Zanello,2011). This what is predicted by the 4N series method. Furthermore, it is found that the inner cluster [M6] comprises of Pd skeletal elements only.

4.

4. F=$Ru_6Pd_6(CO)_{24}^{2-}$:K=6[5]+6[4]-24-1=29, n=6+6=12
K(n)=29(12)
24-29= -5
S=4n-10
K=2n+5
Kp=C^6C[M6]
Kp'=C^6+D^6
Kp'' =C^6(Ru)+D^6(Pd; from observation
VE=14n-10=14[12]-10=158
VE0=2n+2(n=from nucleus)=2[6]+2=14
VE=VE0+12n=14+12[12]=158
vf=6[8]+6[10]+24[2]+2=158

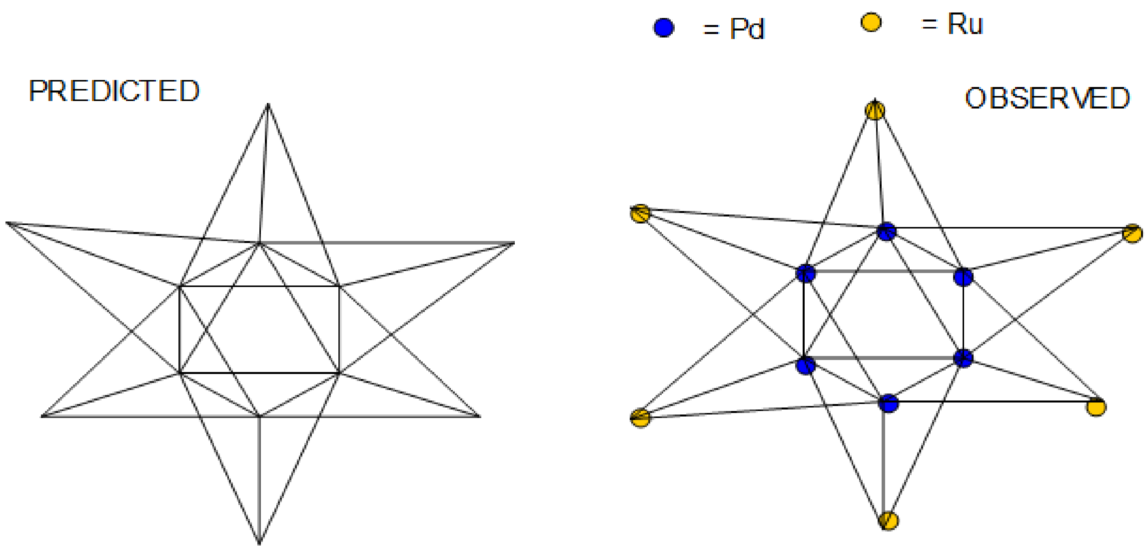


Figure 21. Isomeric graphical structure of Ru6Pd6$(CO)_{24}^{2-}$

5. $Os_{17}(CO)_{36}^{2-}$:VE=17[8]+36[2]+2=210, n=17,VE(n)=210(17)

q=210-14[17]= -28

S=4n-28

K=2n+14=2[17]+14=48

Kp=C^{15}C[M2]

Kp'=C^{15}+D^2

In this case, we have one set of 15 skeletal elements in the outer shell and 2 skeletal elements in the inner shell. The two skeletal elements follow the series S1=4n+2, K=2n-1=2[2]-1=3. Ideally, the two skeletal elements are linked by a triple bond. The outer shell follows the series S2=4n-2(15)=4n-30, K2=2n+15=2[15]+15=45; K1+K2=3+45=48

6. $Os_{20}(CO)_{40}^{2-}$: VE=20[8]+40[2]+2=242,n=20

VE(n)=242(20)

q=VE-14n=242-14[20]= -38

S=4n-38

K=2n+19

$Kp=C^{20}C[M0]$, VE0=2n+2=2[0]+2=2

$Kp'=C^{20}+D^{0}$

This tells us that all the 20 skeletal elements are in the outer shell capping following the series S=4n-2(20)=4n-40 and there is no skeletal element in the nucleus except the 2 electrons. The capping formula has been applied break into 2 groups of skeletal elements of selected clusters.

More examples obtained mainly from literature sources (Felner & Salet, 2007; Dries & NÖth, 2004) are given in Table 9. The extensive reviews by Belyakova and Slovokhotova as well as Mednikov & Dahl provide a wide range of examples (Belyakova & Slovokhotova, 2003; Mednikov & Dahl, 2010) from which the concept of separating the capping elements into two broad groups can be found.

Table 9. A collection of clusters showing their categorization into two groups

	CLUSTER	Kp	OUTER SPHERE	INNER SPHERE
6.	Ga_6R_2:VE=6[3]+2=20 q=20-4[6]= -4 S=4n-4 K=2n+2 $Kp=C^3C[M3]$ $Kp'=C^3+D^3$	$Kp=C^3C[M3]$	3	3
7.	$Ga_9R_6^-$: VE=9[3]+6+1=34,n=9 q=34-4[9]= -2 S=4n-2 K=2n+1 $Kp=C^2C[M7]$ $Kp'=C^2+D^7$	$Kp=C^2C[M7]$	2	7 Pentagonal bipyramid
8.	$Au_9L_8^{3+}$:VE=9[11]+8[2]-3=112,n=9 q=112-14[9]= -14 S=4n-14 K=2n+7 $Kp=C^8C[M1]$ $Kp'=C^8+D^1$	$Kp=C^8C[M1]$	8 TORROIDAL	1
9.	$Au_9L_8^+$:VE=9[11]+8[2]-1=3=114,n=9 q=114-14[9]= -12 S=4n-12 K=2n+6 $Kp=C^7C[M2]$ $Kp'=C^7+D^2$	$Kp=C^7C[M2]$	7 SPHERICAL	2
10.	$Os_{10}(C)(CO)_{24}^{2-}$:VE=10[8]+4+48+2=134,n=10 q=134-14[10]= -6 S=4n-6 K=2n+3 $Kp=C^4C[M6]$ $Kp'=C^4+D^6$	$Kp=C^4C[M6]$	4	6 Octahedral shape
11.	$Ga_{10}R_6$ q=36-40=-4 S=4n-4 K=2n+2 $Kp=C^3C[M7]$ $Kp'=C^3+D^7$	$Kp=C^3C[M7]$	3	7 Pentagonal bipyramid
12.	In_{11}^{7-}:VE=40,n=11 q=VE-4n=40-4[11]= -4 S=4n-4 K=2n+2 $Kp=C^3C[M8]$ $Kp'=C^3+D^8$	$Kp=C^3C[M8]$	3	8
13.	$Rh_{14}(CO)_{26}^{2-}$ VE=14[9]+52+2=180,n=14 q=180-14[14]= -16 S=4n-16 K=2n+8 $Kp=C^9C[M5]$ $Kp'=C^9+D^5$	$Kp=C^9C[M5]$	9	5 Trigonal bipyramid
14.	$G_{19}R_6^-$: VE=19[3]+6+1=64,n=19	$Kp=C^7C[12]$	7	12

	$q=64-4[19]= -12$ $S=4n-12$ $K=2n+6$ $Kp=C^7C[M12]$ $Kp'=C^7+D^{12}$			icosahedron
15.	$Zr_6Cl_{14}L_4$:K=6[7]+14[0.5]-4=45 K(n)=45(20) 40-45= -5 $S=4n-10$ $K=2n+5$ $Kp=C^6C[M14]$ $Kp'=C^6(Zr)+D^{14}(Cl)$	$Kp=C^6C[M14]$	6 Octahdron	14 Capping Cl elements
16.	$Ga_{22}R_8$:VE=22[3]+8=74 74-4[22]= -14 $S=4n-14$ $K=2n+7$ $Kp=C^8C[M14]$ $Kp'=C^8+D^{14}$	$Kp=C^8C[M14]$	8	14
17.	$Ga_{26}R_8^{2-}$:VE=26[3]+8+2=88,n=26 q=VE-4n=88-4[26]= -16 $S=4n-16$ $K=2n+8$ $Kp=C^9C[M17]$ $Kp'=C^9+D^{17}$	$Kp=C^9C[M17]$	9	17
18.	$AS_{21}Ni_{12}^{3-}$:K=21[1.5]+12[4]-1.5=78 n=21+12=33 K(n)=78(33) 66-78= -12 $S=4n-24$ $K=2n+12$ $Kp=C^{13}C[M20]$ $Kp'=C^{13}+D^{20}$ $Kp''=C^1(As)+C^{12}(Ni)+D^{20}(As)$	$Kp=C^{13}C[M20]$	13 12 (Ni) icosahedron, 1(As center)	20 (As) skeletal elements in the outer shell
19.	$Cu_{26}Se_{13}L_{14}$: K=26[3.5]+13[1]-14=90,n=26+13=39 K(n)=90(39) 78-90=-12 $S=4n-24$ $K=2n+12$ $Kp=C^{13}C[M26]$ $Kp'=C^{13}+D^{26}$ $Kp''=C^1(Se)+C^{12}(Cu)+D^{12}(Se)+D^{14}(Cu)$	$Kp=C^{13}C[M26]$	13 Icosahedron centered	26
20.	$Ni_{38}Pt_6(CO)_{48}^{6-}$:K=38[4]+6[4]-48-3= 125,n=44 K(n)=125(44) 88-125= -37 $S=4n-74$ $K=2n+37$ $Kp=C^{38}C[M6]$ $Kp'=C^{38}+D^6$	$Kp=C^{38}C[M6]$	38	6 Octahedron centered
21.	$Al_{69}R_{18}^{3-}$:VE=228 q=228-4[69]= -48 $S=4n-48$ $K=2n+24$ $Kp=C^{25}C[M44]$ $Kp'=C^{25}+D^{44}$	$Kp=C^{25}C[M44]$	25	44

3. Conclusion

The establishment of the base-line valence electron content VE0 strongly underpins the great significance of categorizing clusters into clans and families. The establishment of VE0 enables to directly calculate the cluster valence electrons VE using either the 12N oe the 14N capping series as well as deriving the formulas of the respective clusters. The construction of capping diagrams of clusters and skeletal elements of transition elements has been well established. The black-hole concept of capping electrons may qualitatively explain the difference between metals and non-metals. Some clusters especially the giant ones appear to possess back-holes which have been found to be a characteristic of metallic behavior. The capping formula can be utilized as a simple qualitative guide to separate skeletal elements of capping clusters into two groups, the outer shell and the inner shell. The construction of cluster valence electron trees is a good idea of portraying relationships among clusters of the same clan. Cluster series may simply be regarded as some forms of simple arithmetic progressions with suitable common differences such as 14 for 14N and 12 for 12N series. A capping principle of clusters based upon 12N/14N series has been established.

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