

Graph Theory of Capping Golden Clusters

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Abstract

Skeletal numbers and their valences have been extremely useful in analyzing and categorizing clusters especially boranes, carbonyls, and Zintl ions. This approach is being extended to the analysis and categorization of golden clusters. The newly introduced concept of graphing will also be applied to the clusters. The capping symbol $K_p = C^Y C[M_x]$ which has been restricted to post-closo clusters will be adapted for pre-closo cluster series. The concept of the existence of black holes in the nuclei of capping golden clusters will be introduced and explained.

Keywords: golden clusters, black holes, capping series, de-capping series, skeletal numbers, $K(n)$ series, nuclearity index

1. Introduction

The first golden cluster to be synthesized was $Au_{11}I_3L_7$ in 1968(Mingos, 1984). Since then many more clusters have been synthesized(Cotton & Wilkinson, 1980; Greenwood&Earnshaw,1998;Gimeno,2008;Kilmartin, 2010;Kwok-Ming, 2011, Konishi, 2014).The golden clusters have attracted immense interest among many scientists in terms of trying to understand their geometrical shapes, bonding and potential applications in catalysis and nanotechnology(Corti, et al, 2005;Zhang, et al, 2014). The fascinating shapes of gold have been described by a number of ways, for instance, $Au_4I_2L_4$, tetrahedral; $Au_6L_6^{2+}$, ($L = PPh_3$), octahedral; $Au_8L_8^{2+}$, chair-like centered hexagon; $Au_{13}Cl_2L_{10}^{3+}$, ($L = PMe_2Ph$); icosahedron; $Au_8L_7^{2+}$ and $Au_9L_8^{3+}$; flat, ring, torus or doughnut-shaped(Cotton & Wilkinson, 1980;Greenwood & Earnshaw, 1998). Further descriptions include, centered polyhedral, non-centered polyhedral and exo-attached polyhedral clusters(Konishi,2014). The recent application of the $4n$ series method to the analysis and categorization of golden clusters indicated almost all the clusters with nuclearity index 4 and above belong to the CAPPING SERIES (Kiremire, 2016, 2017). With the development of skeletal numbers and the concept of graph theory of capping series (Kiremire, 2017b, 2017c), it will be interesting to investigate how the golden cluster structures look like under the series graph theory.

2. Results and Discussion

In order to be able to compare and contrast the structures of gold as compared to other clusters, let us compare and contrast the structures of two hypothetical clusters, namely C_6H_{10} and Au_6H_{10} . The K value of C_6H_{10} : $K = 6[2]-5 = 7$; $K(n) = 7(6), S = 4n+10$. In the case of Au_6H_{10} : $K = 6[3.5]-5 = 16$; $K(n) = 16(6)$, $S = 4n-8$, $K_p = C^5C[M_1]$. The calculation of skeletal linkages of clusters has been discussed extensively (Kiremire, 2017d). Let us analyze these cases one at a time.

Ex-1: C_6H_{10} : $K = 6[2]-5 = 7$; $K(n) = 7(6), S = 4n+10$. The symbol $K(n) = 7(6)$ means that the 6 carbon skeletal atoms in the formula are joined by 7 linkages or bonds. One of the possible skeletal isomers is shown as F-1. The skeletal number of carbon [C], $K = 2$, gold, [Au], $K = 3.5$, [H] as a ligand, $K = -0.5$ since it is a 1 electron donor (refer to appendixes 1 and 2). The number of valence electrons can also be derived from the series formula: $Ve = 4n+10 = 4(6)+10 = 34$. This figure can be confirmed from the cluster formula itself: $VF = 6[4]+10 = 34$.

Ex-2: Au_6H_{10} : $K = 6[3.5]-5 = 16$, $K(n) = 16(6)$, $S = 4n-8$, $K_p = C^5C[M_1]$. This symbol means that the cluster is capped in such a way that 5 skeletal elements are surrounding 1 central skeletal atom at the nucleus. In addition, the skeletal framework of 6 golden elements is bound by 16 linkages. Since each capping skeletal element uses 3 linkages, the 5 capping elements means utilizing 15 of the skeletal linkages out of the 16. Since the cluster has one skeletal element {[M1]; n = 1}, then the element obeys the CLOSO series formula $S = 4n+2$ and $K = 2n-1 = 2(1)-1 = 1$. Thus, the skeletal element in the nucleus utilizes 1 skeletal element and the 5 capping atoms consume 15 skeletal elements giving us a total of $15+1 = 16$. For categorization, we can use $S = 4n+q$ for main group and transition elements. However for calculating the number of valence electrons we have to use $Ve = 14n+q$ equation. In this case, the number of valence electrons will be given by $Ve = 14n-8 = 14(6)-8 = 76$. We can verify this from the cluster formula $F = Au_6H_{10}$; $VF =$

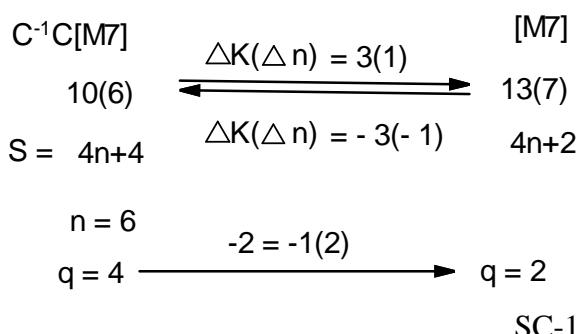
$6[11] + 10 = 76$. Since $K_p = C^5C[M1]$, the capping symbol can guide us to sketch a skeletal isomeric structure, F-2.

Ex-3: Zn_6H_{10} : $K = 6[3]-5 = 13$; $K(n) = 13(6)$, $S = 4n-2$, $K_p = C^2C[M4]$. This is a bi-capped tetrahedron. Its possible isomeric structure has been proposed F-3.

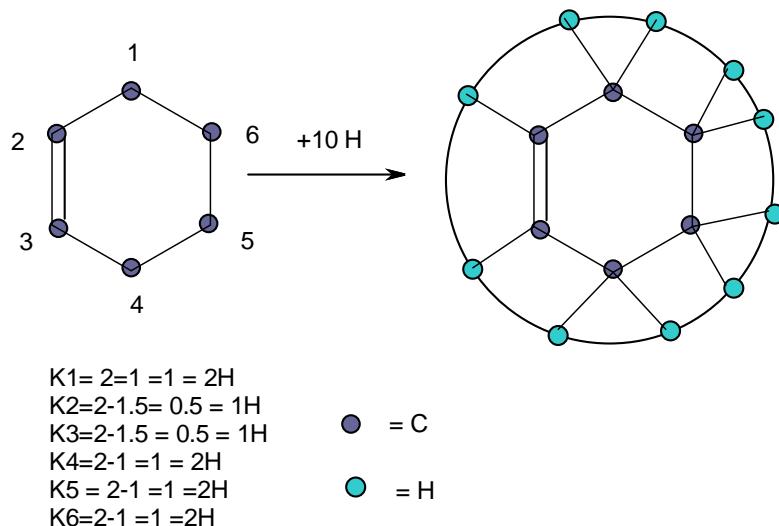
Ex-4: B_6H_{10} : $K = 6[2.5]-5 = 10$; $K(n) = 10(6)$, $S = 4n+4(q = 4)$. The closo series is given by $S = 4n+2(q = 2)$. Since the ordinary series, q runs in the multiples of 2, $S = 4n+4$ is a step before $S = 4n+2$. If we follow the Rudolph type of capping series, then the closo above B_6H_{10} will have a K value of 13 and $n = 7$. Hence, its closo cluster parameter will be $K(n) = 13(7) = [M7]$. Since capping clusters after $[M7]$ are expressed as $K_p = C^yC[Mx]$, then the de-capping series can be expressed as $K_p = C^{-y}C[Mx]$. Therefore, the cluster $K(n) = 10(6)$, can be expressed as $K_p = C^{-1}C[M7]$. According to this approach, this symbol means, its $K(n)$ is one step below the closo base, that is, $\Delta K = -3$, and $\Delta n = -1 \equiv \Delta K(\Delta n) = -3(-1)$. We can express this idea diagrammatically, SC-1. This means that by comparing the q value of a cluster and that of the ‘standard reference’ closo system, we can determine the relative positions of the $K(n)$ values and hence numerically categorize the cluster, in this case $10(6)$, $K_p = C^{-1}C[M7]$.

Ex-5: B_5H_9 and Ex-6: B_4H_{10} were numerically categorized in the same way.

$$S = 4n+q$$



C_6H_{10} : $K=6[2]-10(0.5) = 7$, $K(n) = 7(6)$, $S = 4n+10$; $Ve = 4(6)+10 = 34$, $VF = 6[4]+10 = 34$

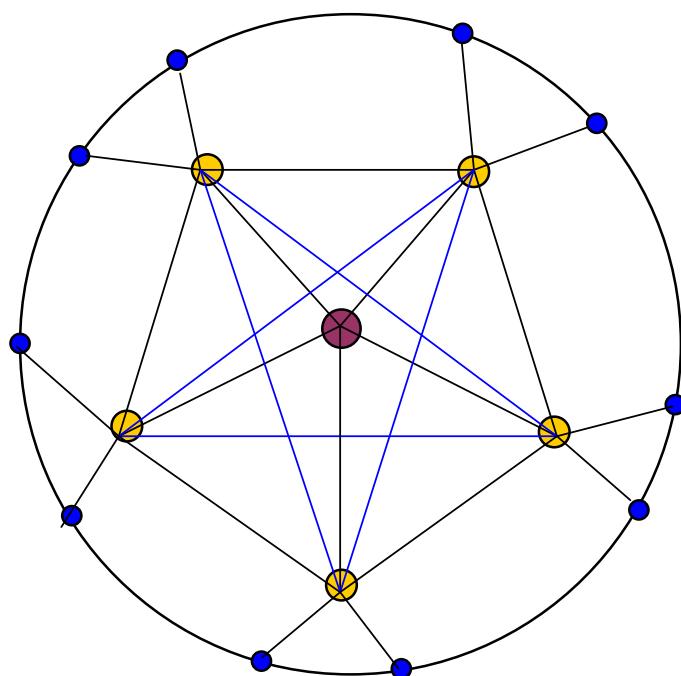


Is $K(n) = 10(6)$ below [M7]? We can test this by a simple check on the flow of $K(n)$ numbers.

[M7] means, $S = 4n+2(n = 7)$. Hence $K = 2n-1 = 2(7)-1 = 13$ and so $K(n) = 13(7)$ for [M7].

[M7] lower series will be as follows starting with $[M7] = 13(7) \rightarrow 10(6) \rightarrow 7(5) \rightarrow 4(4) \rightarrow 1(3)$. According to the historical terminology 13(7) will correspond to a CLOSO system, 10(6), NIDO; 7(5), ARACHNO; 4(4), HYPHO; and 1(3), KLADO system. The symbol [M7] will also represent the borane cluster $B_7H_7^{2-}$. Hence, $K(n) = 10(6)$ is just one step below the closo system [M7] and corresponds to a nidoborane cluster B_6H_{10} .

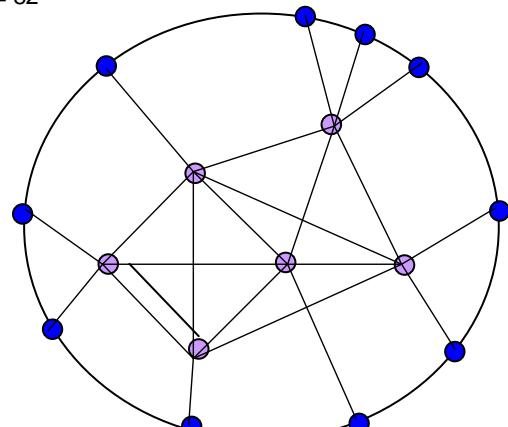
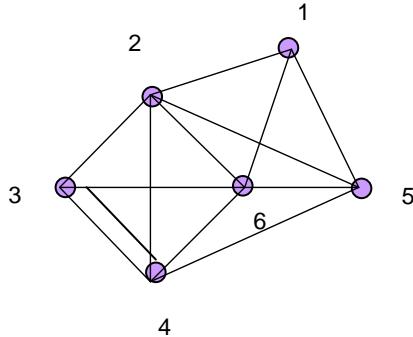
According to the series method, $K(n) = 16(6)$, $K_p = C^5C[M1]$. This means it belongs to the group or a clan of clusters which have got 1 skeletal element in the nucleus. Thus, $K(n) = 16(6)$ parameter will be found to be a member of [M1] - based numbers. This can be seen to be the case as indicated in the [M1] series.



Zn_6H_{10} : $K = 6[3]-5 = 13$; $K(n) = 13(6)$, $S = 4n-2$, $K_p = C^2C[M4]$

$$Ve = 14n-2 = 14(6)-2 = 82, VF = 6[12]+10 = 82$$

$$[M4], K=2n-1 = 2(4)-1 = 7$$



$$K1=1[3]-1.5 = 1.5 = 3H$$

$$K2=1[3]-2.5=0.5= 1H$$

$$K3=1[3]-2= 1= 2H$$

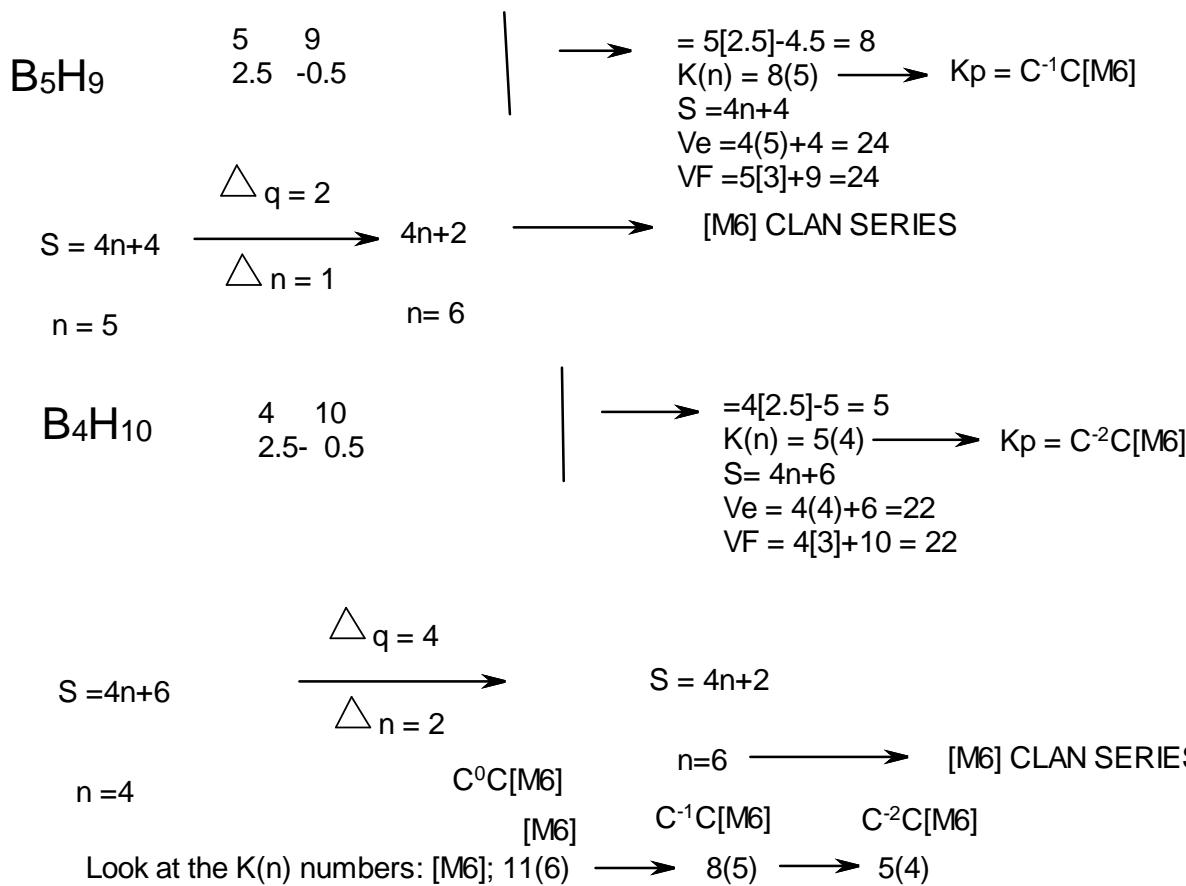
$$K4=1[3]-2.5= 0.5 = 1H$$

$$K5=1[3]-2=1 = 2H$$

$$K6=1[3]-2.5= 0.5 = 1H$$

Is $K(n) = 13(6)$ a member of $[M4]$ series of numbers?. Let us check it out.

$K(n) = 13(6)\{S = 4n-2, K_p = C^2C[M4]\} \rightarrow 10(5)\{S = 4n+0, K_p = C^1C[M5]\} \rightarrow 7(4)\{S=4n+2\}$. The parameter $K(n) = 7(4) = [M4]$.



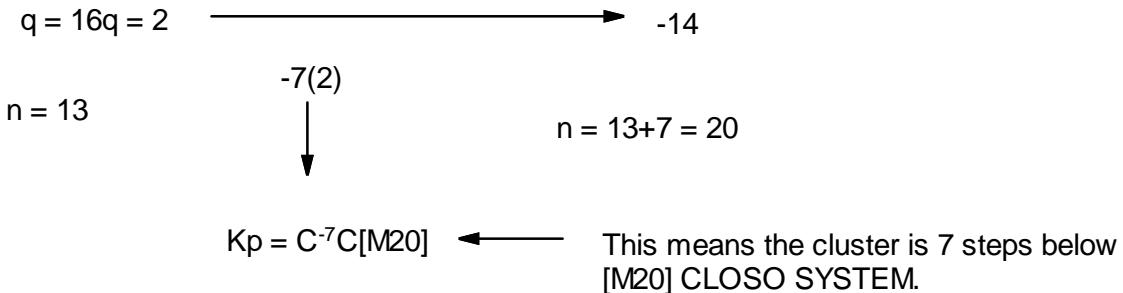
1-2: ASPIRIN- PAIN KILLER, FORMULA, $C_9H_8O_4$

SKELETAL ELEMENTS, [C], [O] AND [H] LIGAND

$$K = 9[2]+4[1]-8(0.5) = 18$$

$$K(n) = 18(13)$$

$$S = 4n+16(n = 13)$$



[M20], $K = 2n-1 = 2(20)-1 = 39$, $K(n) = 39(20) \rightarrow 36(19) \rightarrow 33(18) \rightarrow 30(17) \rightarrow 27(16) \rightarrow 24(15) \rightarrow 21(14) \rightarrow 18(13)$

SC-4

1-3: QUININE - $C_{20}H_{24}N_2O_2$

In this example, let us consider [H] as a ligand and the rest as skeletal elements. Its K value is given by $K=20[2]+2[1.5]+2[1]-24(0.5) = 33$; $K(n) = 33(24)$, $S = 4n+30$. In this case $q = 30$ and we have to compare this with $q = 2$ for a closo system. That is,

$q = 30 \rightarrow q = 2$. The gap is 28 or we must subtract 28 from 30 to arrive at $q = 2$. Hence $\Delta q = -28 = -14(2)$. In terms of series, it means we have to go down numerically by 14 steps corresponding to an increase in n value by 14. Hence, the new $n = 24+14 = 38$. This means the CLOSO system will correspond to $n = 38 \rightarrow [M38]$. Similarly, the quinine formula itself will be at 14 steps below the [M38] closo system. Therefore its symbol is appropriately set at $K_p = C^{-14}C[M38]$. We can test this from the flow of [M38] K(n) numbers, SC-5;

$[M38] \rightarrow 75(38) \rightarrow 72(37) \rightarrow 69(36) \rightarrow 66(35) \rightarrow 63(34) \rightarrow 60(33) \rightarrow 57(32) \rightarrow 54(31) \rightarrow 51(30) \rightarrow 48(29) \rightarrow 45(28) \rightarrow 42(27) \rightarrow 39(26) \rightarrow 36(25) \rightarrow 33(24)$

SC-5

The rest of the examples we can just demonstrate the categorization and the flow of K(n) number series.

1-4: $Cp_4Ni_4B_4H_4$; $K = 4[4]+4[2.5]-4(2.5)-4(0.5) = 14$, $K(n) = 14(8)$, $S = 4n+4$; $q = 4 \rightarrow q = 2$. This means, the cluster is one step below the CLOSO system. Hence, $K_p = C^{-1}C[M9]$. This is a NIDO cluster.

1-5: $Al_{77}R_{10}^-$: $K = 77[2.5]-5-0.5 = 187$; $K(n) = 187(77)$, $S = 4n-66$, $K_p = C^{34}C[M43]$. This is a huge cluster with a large nucleus of 43 skeletal elements capped by 34 skeletal elements. Now, let us see the flow of the K(n) numbers downwards, SC-6.

$187(77) \rightarrow 184(76) \rightarrow 181(75) \rightarrow 178(74) \rightarrow 175(73) \rightarrow 172(72) \rightarrow 169(71) \rightarrow 166(70) \rightarrow 163(69) \rightarrow 160(68) \rightarrow 157(67) \rightarrow 154(66) \rightarrow 151(65) \rightarrow 148(64) \rightarrow 145(63) \rightarrow 142(62) \rightarrow 139(61) \rightarrow 136(60) \rightarrow 133(59) \rightarrow 130(58) \rightarrow 127(57) \rightarrow 124(56) \rightarrow 121(55) \rightarrow 18(54) \rightarrow 115(53) \rightarrow 112(52) \rightarrow 109(51) \rightarrow 106(50) \rightarrow 103(49) \rightarrow 100(48) \rightarrow 97(47) \rightarrow 94(46) \rightarrow 91(45) \rightarrow 88(44) \rightarrow 85(43)$

$K(n) = 85(43)$, $S = 4n+2$; CLOSO SYSTEM. Hence, $K(n) = 187(77) \rightarrow K_p = C^{34}C[M43]$ is in line with the K(n) number series.

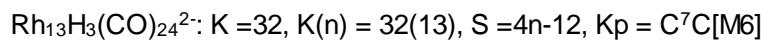
SC-6

1-6: $Sb_7Ni_3(CO)_3^{3-}$: $K = 7[1.5+3[4]-3-1.5 = 18$; $K(n) = 18(10)$, $S = 4n+4$; $K_p = C^{-1}C[M11]$. This is a NIDO cluster – a derivative from [M11] which corresponds to $B_{11}H_{11}^{2-}$ closo cluster.

1-7: $Rh_{13}H_3(CO)_{24}^{2-}$: $K = 13[4.5]-1.5-24-1 = 32$; $K(n) = 32(13)$, $S = 4n-12$, $K_p = C^7C[M6]$. Let us look at the flow of the K(n) numbers and then the skeletal graph of the cluster.

$32(13) \rightarrow 29(12) \rightarrow 26(11) \rightarrow 23(10) \rightarrow 20(9) \rightarrow 17(8) \rightarrow 14(7) \rightarrow 11(6)$

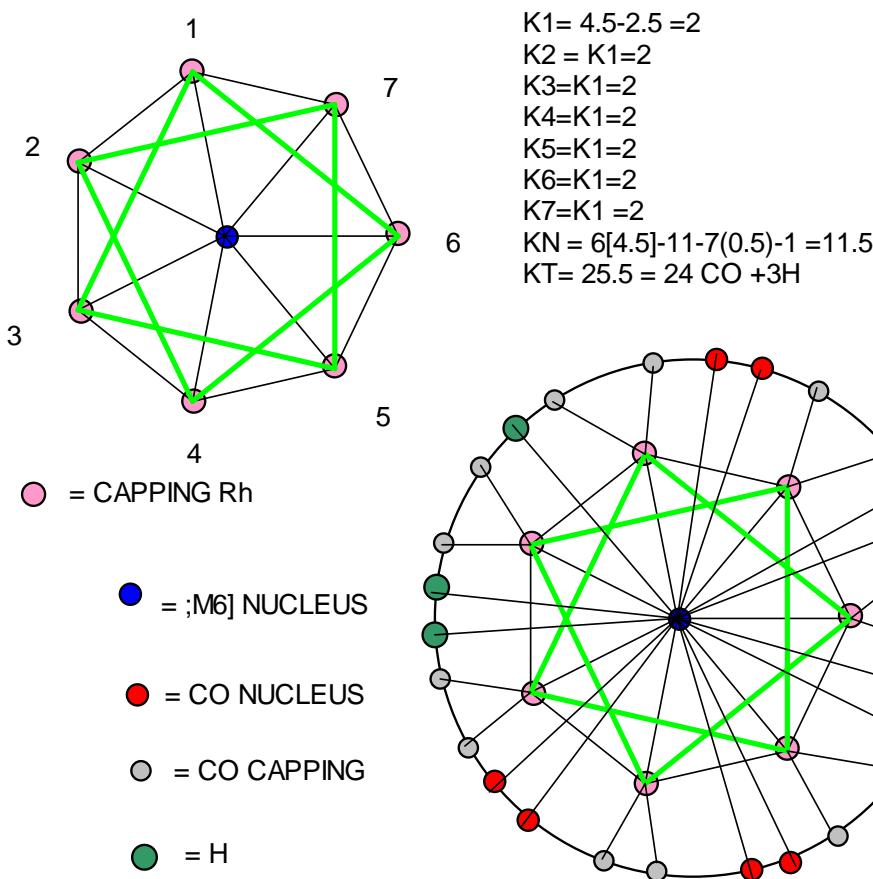
This clearly agrees with the flow of the K(n) numbers and with the [M6] series below. The cluster symbol $K_p = C^7C[M6]$ means that the overall cluster has an O_h nucleus of 6 skeletal elements surrounded by 7 capping skeletal elements. The sketch of the possible isomeric skeletal graph F-5



$$[M6], K = 2n-1 = 2(6)-1 = 11$$

Rh(K=4.5, V=9)

$$\text{SKELETAL LINKAGES} = 7+7+7+[M6] = 21+11 = 32$$



When we analyze more closely, it is quite clear that chemical elements, fragments, molecular formulas and clusters comprising of the main group and transition metals can readily be categorized using skeletal numbers. Therefore the clusters such as boranes, carboranes, metalloboranes, transition metal carbonyls, Zintl ion clusters and others all belong to one universe of clusters which obey a simple cluster formula $S = 4n+q$ ($q > 0$, non-capping clusters; $q \leq 0$, capping clusters) and a simple parameter $K(n)$. It has been proposed that the clusters are best grouped according to the CLOSO NUCLEAR SYSTEM [Mx]. Although the golden clusters are usually centered around the closo nuclei [M1] and [M2] series, a number of examples of [Mx] series have been provided to allow readers to have familiarity with the beautiful flow of $K(n)$ numbers. The important Rudolph correlation system set up about 40 years ago is a subset of the universe of $K(n)$ numbers. A sample of selected [Mx] series SRS -1 are given below for illustrations and a selected collection of golden clusters are analyzed using skeletal numbers and their skeletal graphs mixed with a few non-golden clusters for comparison are shown F-6 to F-34

[M0]Series:

-1(0)→2(1)
 →5(2)→8(3)→11(4)→14(5)→17(6)→20(7)→23(8)→26(9)→29(10)→32(11)→35(12)→38(13)→41(14)→44(15)→47(16)→50(17)→53(18)→56(19)→59(20)→62(21)→65(22)→68(23)→71(24)→74(25)→77(26)→80(27),...

BELOW [M0]

NEGATIVE K(n) VALUES

[M1]Series:**1(1)**→4(2)→7(3)→10(4)→13(5)→16(6)→19(7)→22(8)→25(9)→28(10)→31(11)→34(12)→37(13)→40(14)→43(15)→46(16)→49(17)→52(18)→55(19)→58(20)→61(21)→64(22)→67(23)→70(24),.....

BELOW [M1]

NEGATIVE K(n) VALUES

[M2] Series:

3(2)→**6(3)**→9(4)→12(5)→15(6)→18(7)→21(8)→24(9)→27(10)→30(11)→33(12)→36(13)→39(14)→42(15)→45(16)→48(17)→51(18)→54(19)→57(20)→60(21)→63(22)→66(23)→69(24)→72(25),

BELOW [M2]

3(2)→0(1)

[M3]Series

5(3)→8(4) →11(5) →14(6) →17(7)
 →20(8)→23(9)→26(10)→29(11)→32(12)→35(13)→38(14)→41(15)→44(16)→47(17)→50(18)→53(19)→56(20)→59(21)→62(22)→65(23)→68(24)→71(25),....

BELOW [M3]

5(3)→2(2)

[M4]Series

7(4)→10(5)→13(6)→16(7)→19(8)→22(9)→25(10)→28(11)→31(12)→34(13)→37(14)→40(15)→43(16)→46(17)→49(18)→52(19)→55(20)→58(21)→61(22)→64(23)→67(24)→70(25),

BELOW [M4]

7(4)→4(3)→1(2)

[M5]Series:

9(5)→12(6)→15(7)→18(8)→21(9)→24(10)→27(11)→30(12)→33(13)→36(14)→39(15)→42(16)→45(17)→48(18)→51(19)→54(20)→57(21)→60(22)→63(23)→66(24)→69(25)→71(26)→74(27)→77(28)→80(29), ...

BELOW [M5]

9(5)→6(4)→3(3)→0(2)

[M6]Series:

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),....

BELOW [M6]

11(6)→8(5)→5(4)→2(3)

[M7]Series:

13(7)→16(8)→19(9)→22(10)→25(11)→28(12)→31(13)→34(14)→37(15)→40(16)→43(17)→46(18)→49(19)→52(20)→55(21)→58(22)→61(23)→64(24)→67(25)→70(26)→73(27)→76(28)→79(29)→82(30), ...

BELOW [M7]

13(7)→10(6)→7(5)→4(4)→1(3)

[M8]Series:

15(8)→18(9)→21(10)→24(11)→27(12)→30(13)→33(14)→36(15)→39(16)→42(17)→45(18)→48(19)→51(20)→54(21)→57(22)→60(23)→63(24)→66(25)→69(26)→72(27)→75(28)→78(29)→81(30), ..

BELOW [M8]

15(8)→12(7)→9(6)→6(5)→3(4)→0(3)

[M9]Series:

17(9)→20(10)→23(11)→26(12)→29(13)→32(14)→35(15)→38(16)→41(17)→44(18)→47(19)→50(20)→53(21)→56(22)→59(23)→62(24)→65(25)→68(26)→71(27)→74(28)→77(29)→80(30),...

BELOW [M9]

17(9)→14(8)→11(7)→8(6)→5(5)→2(4)

[M10]Series:

19(10)→22(11)→25(12)→28(13)→31(14)→34(15)→37(16)→40(17)→43(18)→46(19)→49(20)→52(21)→55(22)→58(23)→61(24)→64(25)→67(26)→70(27)→73(28)→76(29)→79(30)→82(31),...

BELOW [M10]

19(10)→16(9)→13(8)→10(7)→7(6)→4(5)→1(4)

[M11]Series:

21(11)→24(12)→27(13)→30(14)→33(15)→36(16)→39(17)→42(18)→45(19)→48(20)→51(21)→54(22)→57(23)→60(24),...

BELOW [M11]

21(11)→18(10)→15(9)→12(8)→9(7)→6(6)→3(5)→0(4)

[M12]Series:

23(12)→26(13)→29(14)→32(15)→35(16)→38(17)→41(18)→44(19)→47(20)→50(21),

BELOW [M12]

23(12)→20(11)→17(10)→14(9)→11(8)→8(7)→5(6)→2(5)

[M13]Series

25(13)→28(14)→31(15)→34(16)→37(17)→40(18)→43(19)→46(20)→49(21)→52(22),...

BELOW [M13]

25(13)→22(12)→19(11)→16(10)→13(9)→10(8)→7(7)→4(6)→1(5)

[M-1] Series

-3(-1)→0(0)→3(1)→6(2)→9(3)→12(4)→15(5)→18(6)→21(7)→24(8)→27(9)→30(10),....

[M-2] Series

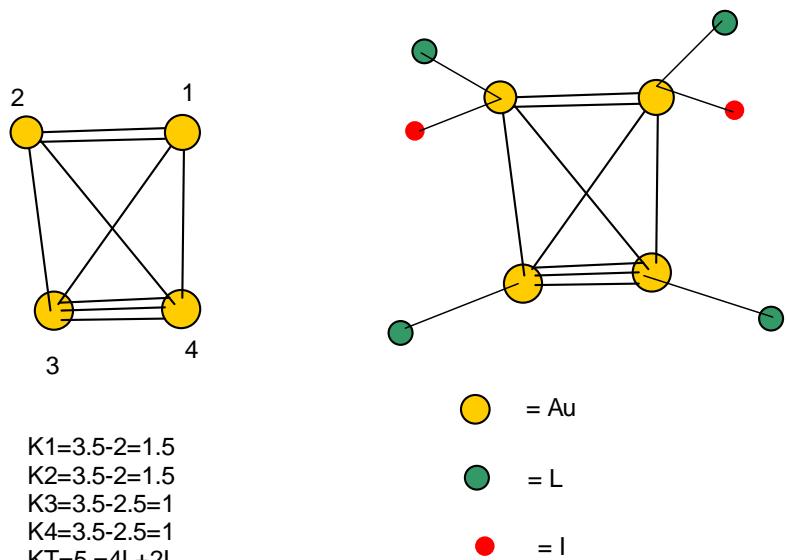
-5(-2)→-2(-1)→5(0)→7(1)→10(2)→13(3)→16(4)→19(5)→21(6)→24(7)→27(8)→30(9)→33(10), ...

[M-3] Series

-7(-3)→-4(-2)→-1(-1)→2(0)→5(1)→8(2)→11(3)→14(4)→17(5)→20(6)→23(7)→26(8)→29(9)→32(10),

SRS-1

$\text{Au}_4\text{L}_4\text{I}_2$: $K = 4[3.5]-4-1 = 9$; $K(n) = 9(4)$, $S = 4n-2$, $K_p = C^2C[M2]$

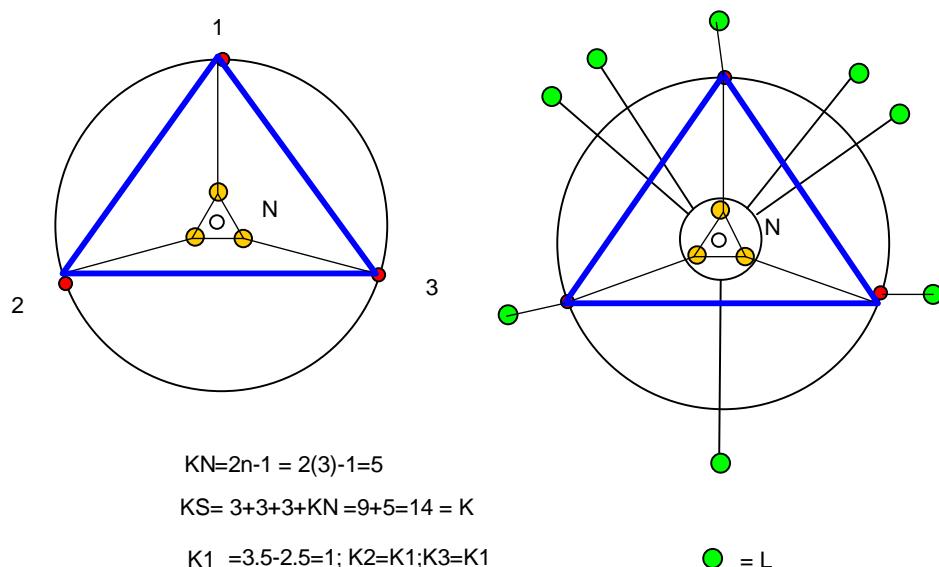


$$Ve = 14n-2 = 14(4)-2 = 54; VF = 4[11]+8+2 = 54$$

Ve = valence electrons, VF = valence electrons from cluster formula

$K(n) = 9(4)$ belongs to [M2]series.

$\text{Au}_6\text{L}_8^{2+}$: $K = 14$; $K_p = C^3C[M3]$



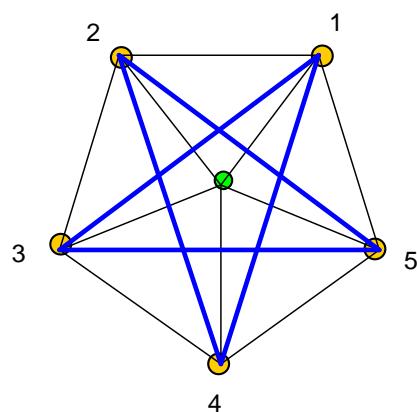
$K(n) = 14(6)$ belongs to [M3] series

$\text{Au}_6\text{L}_6^{2+}$: $K = 6[3.5]-6+1 = 16$; $K(n) = 16(6)$, $S = 4n-8$, $K_p = C^5C[M1]$

$V_e = 14n-8 = 14(6)-8 = 76$; $VF = 6[11]+12-2 = 76$

[M1], $S = 4n+2$, $K = 2n-1 = 2(1)-1 = 1$

$SL = 5+5+5+1 = 16$



$$K_1 = 3.5 - 2.5 = 1$$

$$K_2 = K_1 = 1$$

$$K_3 = K_1 = 1$$

$$K_4 = K_1 = 1$$

$$K_5 = K_1 = 1$$

$$KN = 1[3.5 + 1 - 2.5 - 1] = 1$$

$$KT = 6 = 6L$$

● = CAPPING Au

● = NUCLEAR Au

● = L

$K(n) = 16(6)$ belongs to [M1] series

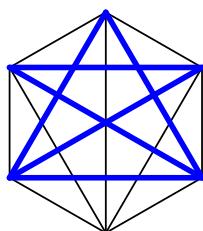
ISOMERIC STRUCTURE OF $\text{Au}_6\text{L}_6^{2+}$

$$K = 6[3.5]-6+1 = 16$$

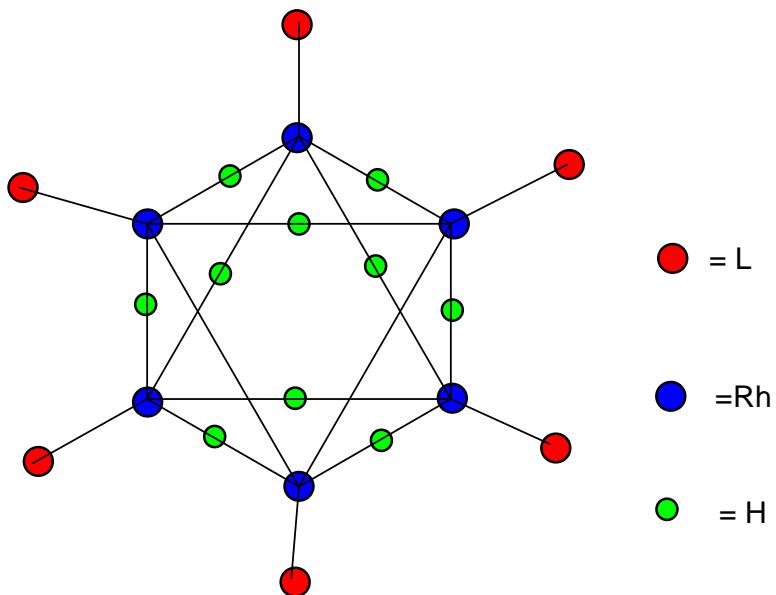
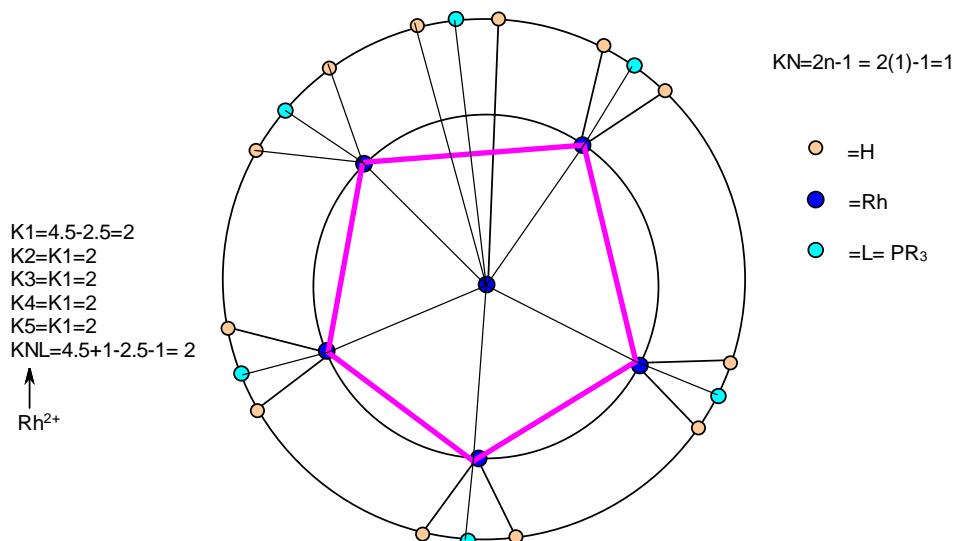
$$K(n) = 16(6)$$

$$S = 4n-8$$

$$K_p = C^5C[M1]$$

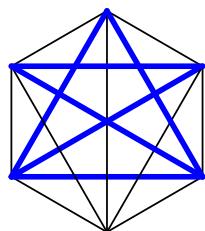


$\text{Rh}_6\text{L}_6\text{H}_{12}^{2+}$: $K = 6[4.5] \cdot 6 \cdot 6 + 1 = 16$, $K(n) = 16(6)$, $S = 4n - 8$, $K_p = C^5 C[M1]$
 $V_e = 14n - 8 = 14(6) - 8 = 76$, $VF = 6[9] + 12 + 12 - 2 = 76$

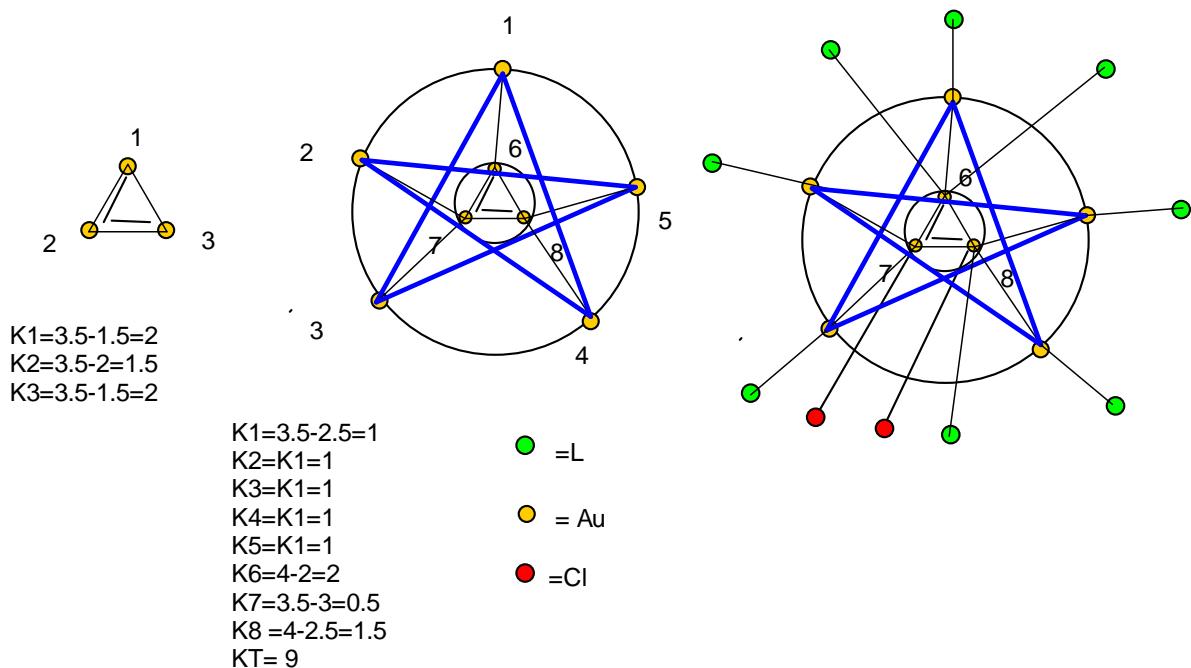


ISOMERIC SKELETAL SHAPE OF $\text{Rh}_6\text{L}_6\text{H}_{12}^{2+}$.

$$\begin{aligned}
 K &= 6[3.5]-6+1 = 16 \\
 K(n) &= 16(6) \\
 S &= 4n-8 \\
 K_p &= C^5 C[M1]
 \end{aligned}$$

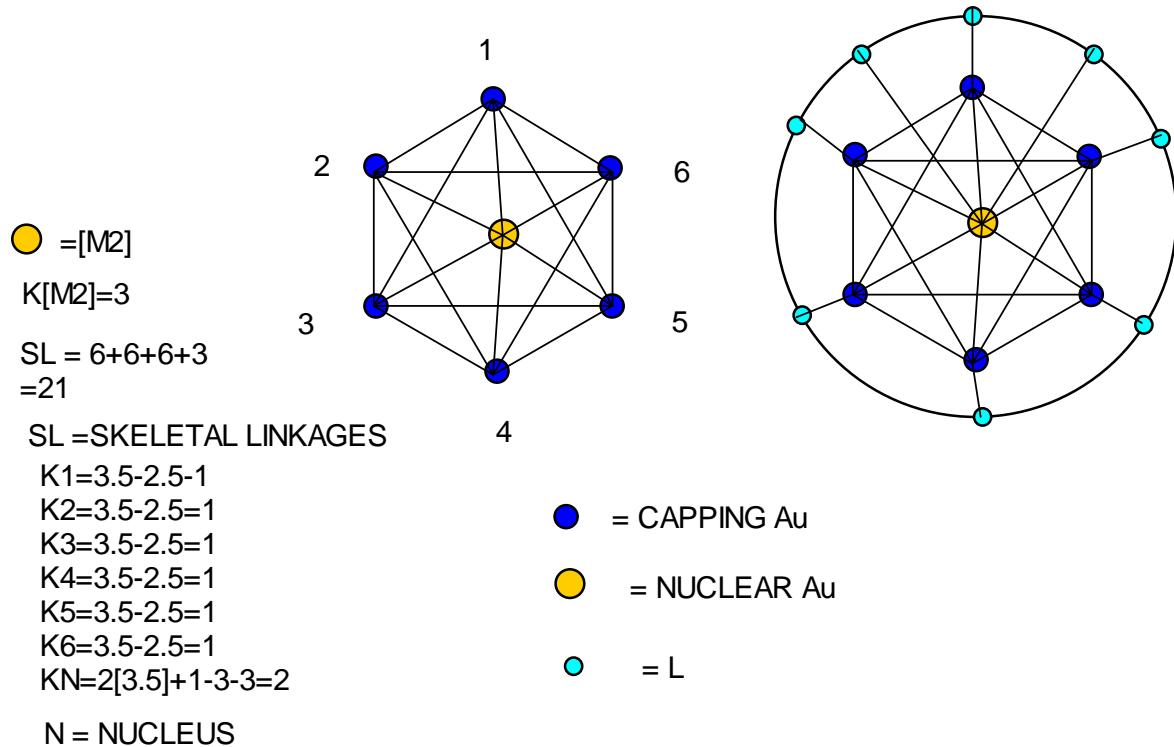


$\text{Au}_8\text{L}_8\text{Cl}_2^{2+}$: $K(n) = 20(8)$, $K_p = C^5 C[M3]$



$K(n) = 20(8)$ belongs to [M3] series

$\text{Au}_8\text{L}_8^{2+}$: $K = 21(8)$, $K_p = C^6C[M2]$



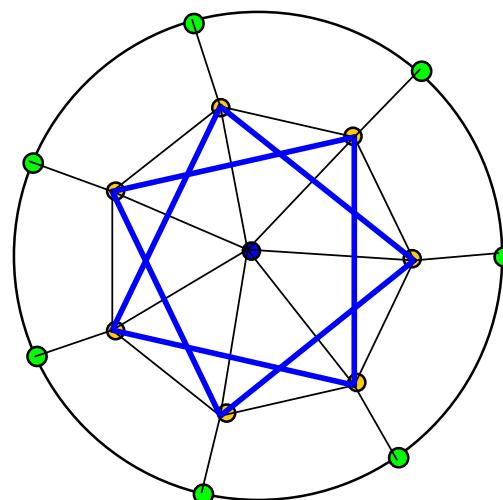
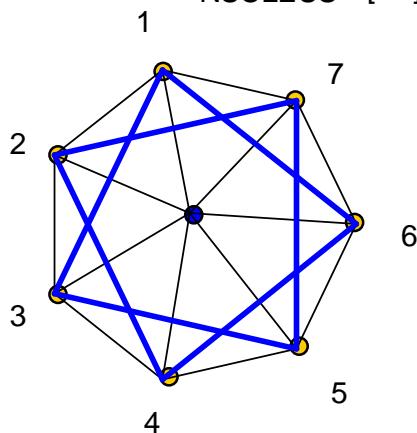
$K(n) = 21(8)$ belongs to [M2] series

$\text{Au}_8\text{L}_7^{2+}$: $K(n) = 22(8)$, $K_p = C^7C[M1]$ $[M1]$, $S = 4n+2$, $K=2n-1 = 2(1)-1 = 1$

$K1=3.5-2.5=1$, $K2=1$, $K3=1$, $K4=1$, $K5=1$, $K6=1$, $K7=1$

$KS = 7+7+7+1=22$ ← SKELETAL LINKAGES

NUCLEUS [M1]



$$KN = 1[3.5] + 1 - 3.5 - 1 = 0$$

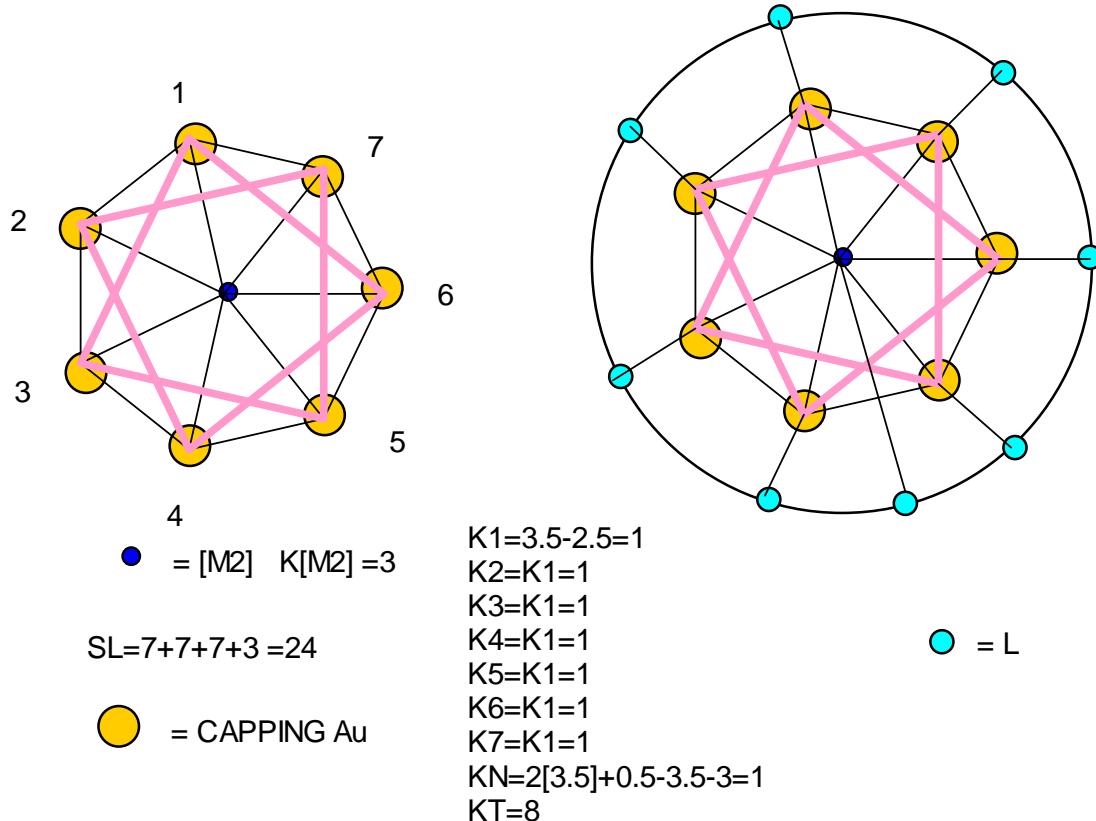
● = CAPPING Au

● = L

$K(n) = 22(8)$ belongs to [M1] series

$\text{Au}_9\text{L}_8^{+1}$: $K = 9[3.5]-8+0.5=24$; $K(n) = 24(9)$, $S=4n-12$, $K_p = C^7C[M2]$

$V_e = 14n-12 = 14(9)-12 = 114$; $VF = 9[11]+16-1 = 114$

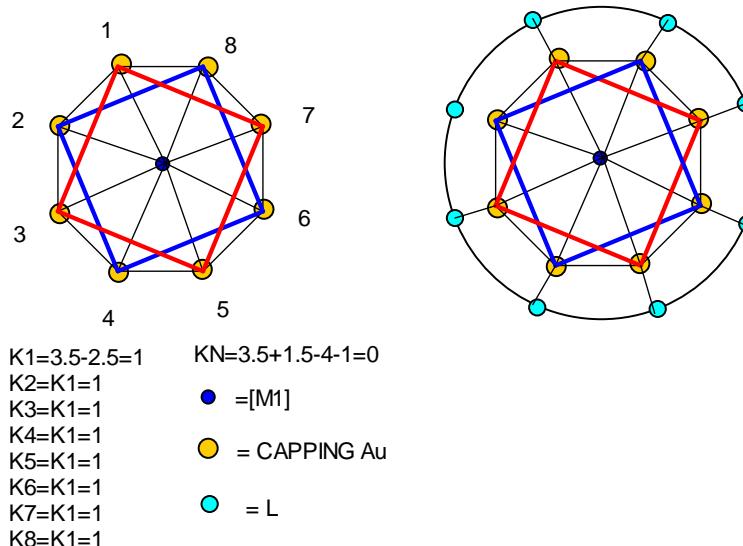


$K(n) = 24(9)$ belongs to [M2] series.

$\text{Au}_9\text{L}_8^{3+}$: $K = 9[3.5]-8+1.5=25$; $K(n) = 25(9)$, $S = 4n-14$, $K_p = C^8C[M1]$

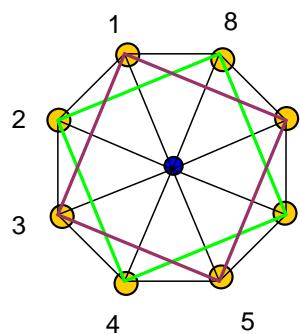
$V_e = 14n-14 = 14(9)-14 = 112$, $VF = 9[11]+16-3 = 112$ $[M1], S = 4n+2, K = 2n-1 = 2(1)-1 = 1$

$SL = 8+8+8+1 = 25$

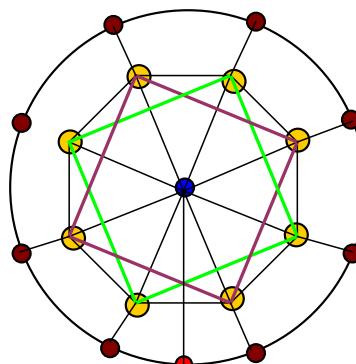


$K(n) = 25(9)$ belongs to [M1] series

$\text{Au}_{10}\text{L}_8\text{Cl}^{+1}$: $K = 10[3.5] - 8 - 0.5 + 0.5 = 27$; $K(n) = 27(10)$, $S = 4n - 14$, $K_p = C^8 C[M2]$ $[M2]$, $S = 4n + 2$, $K = 2n - 1$
 $= 2(2) - 1 = 3$



$$\begin{aligned} K1 &= 3.5 - 2.5 = 1 \\ K2 &= K1 = 1 \\ K3 &= K1 = 1 \\ K4 &= K1 = 1 \\ K5 &= K1 = 1 \\ K6 &= K1 = 1 \\ K7 &= K1 = 1 \\ K8 &= K1 = 1 \\ KN &= 2[3.5] + 0.5 - 4 - 3 = 0.5 \\ KT &= 8.5 \end{aligned}$$

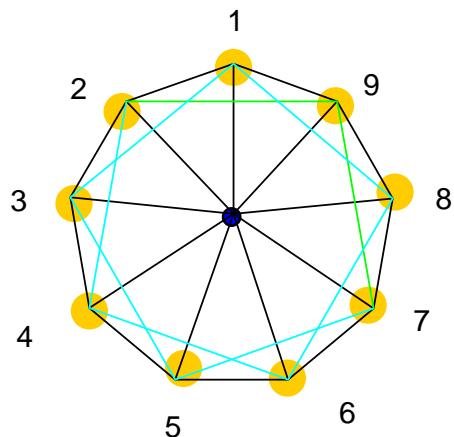


- = $[M2]$
- = L
- = CAPPING Au
- = Cl

$K(n) = 27(10)$ belongs to $[M2]$ series.

$\text{Au}_{10}\text{L}_6\text{Cl}_3^{+1}$: $K = 10[3.5]-6-1.5+0.5 = 28(10)$, $S = 4n-16$, $K_p = \text{C}^9\text{C}[\text{M}1]$ $[\text{M}1]$, $K = 1$

$V_e = 14n-16 = 14(10)-16 = 124$; $VF = 10[11]+12+3-1 = 124$



$$SL = 9+9+9+1 = 28$$

● = $[\text{M}1]$

○ = CAPPING Au

$$K_1 = 3.5 - 2.5 = 1$$

$$K_2 = K_1 = 1$$

$$K_3 = K_1 = 1$$

$$K_4 = K_1 = 1$$

$$K_5 = K_1 = 1$$

$$K_6 = K_1 = 1$$

$$K_7 = K_1 = 1$$

$$K_8 = K_1 = 1$$

$$K_9 = K_1 = 1$$

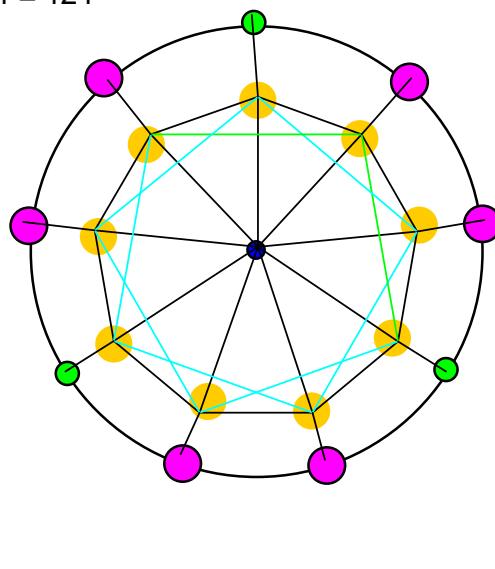
$$K_{10} = K_1 = 1$$

$$KN = 3.5 + 0.5 - 4.5 - 1 = -1.5$$

← BLACKHOLE NUCLEUS

$$KT = 9 - 1.5 = 7.5 = 6L + 3Cl$$

$K(n) = 28(10)$ belongs to $[\text{M}1]$ series.

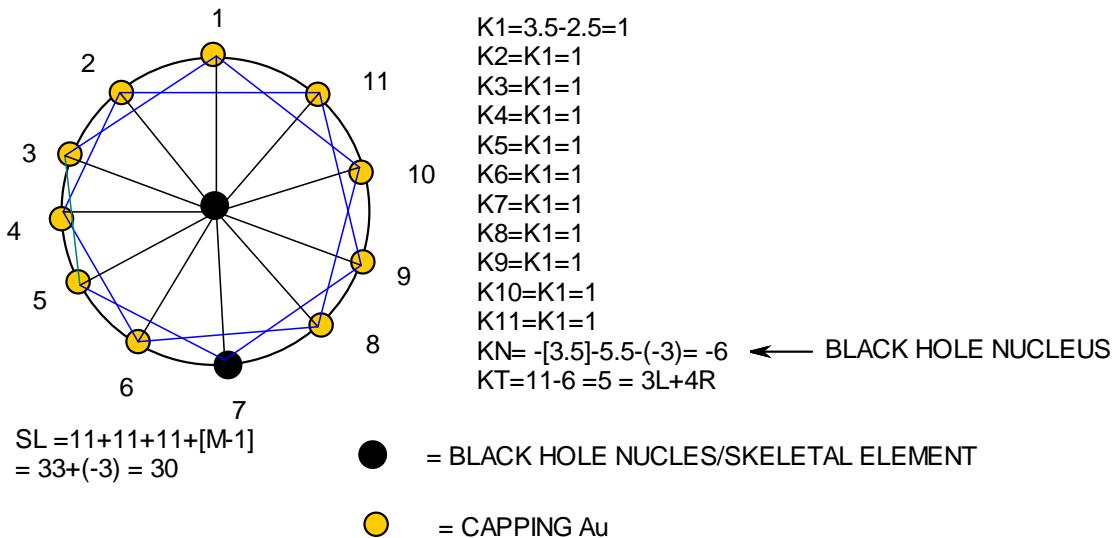


● = L

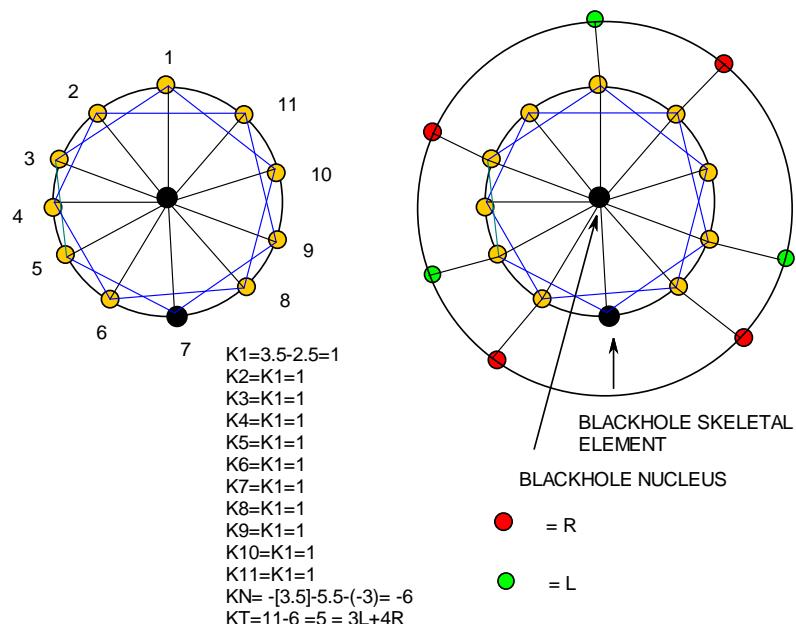
● = Cl

$\text{Au}_{10}\text{L}_3\text{R}_4$: $K = 10[3.5]-3-2 = 30(10)$, $S=4n-20$, $K_p = \text{C}^{11}\text{C}[\text{M}-1]$

$V_e = 14n-20 = 14(10)-20 = 120$, $VF = 10[11]+6+4 = 120$
[M-1], $S = 4n+2$, $K = 2n-1 = 2(-1)-1 = -3$

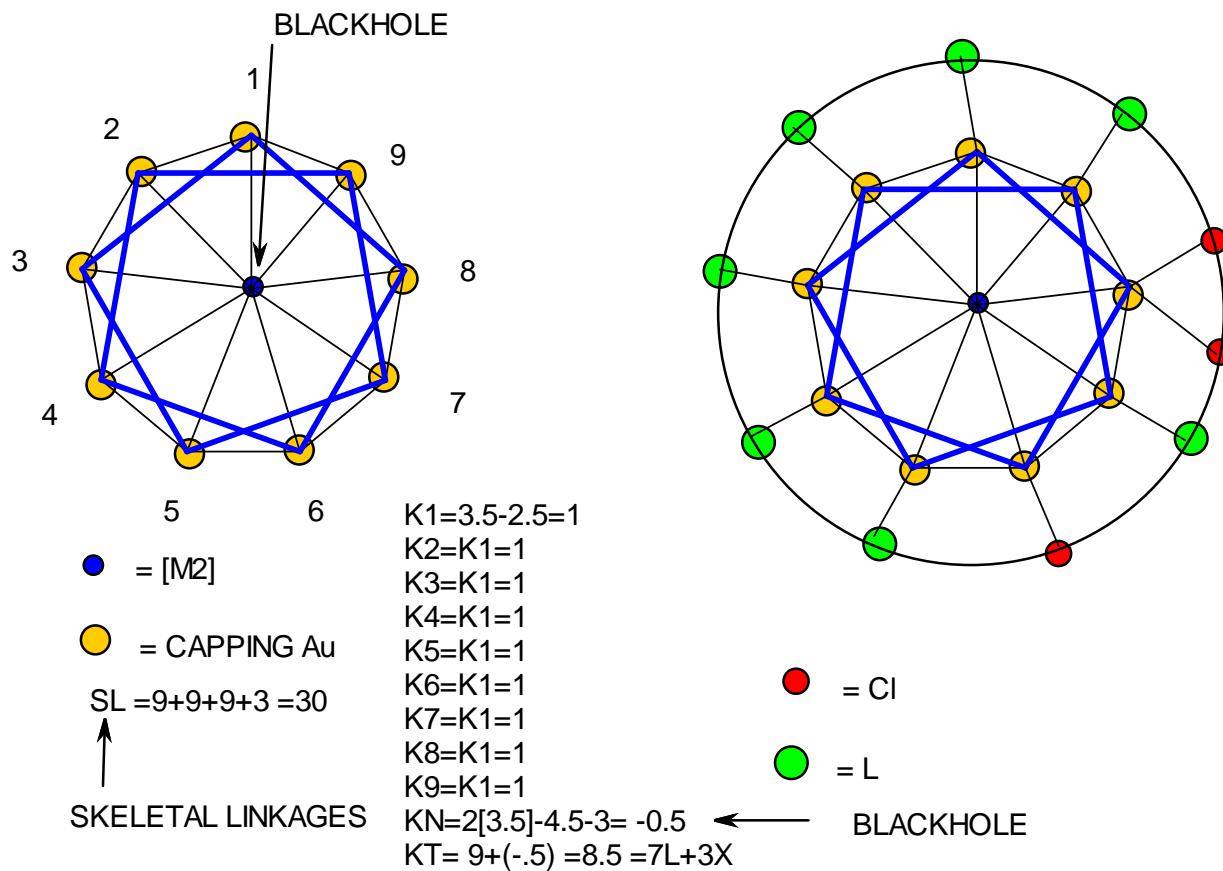


$K(n) = 30(10)$ belongs to [M-1] series.



$\text{Au}_{11}\text{L}_7\text{X}_3$: $K = 11[3.5]-7-1.5 = 30$, $K(n) = 30(11)$, $S = 4n-16$, $K_p = C^9C[M2]$

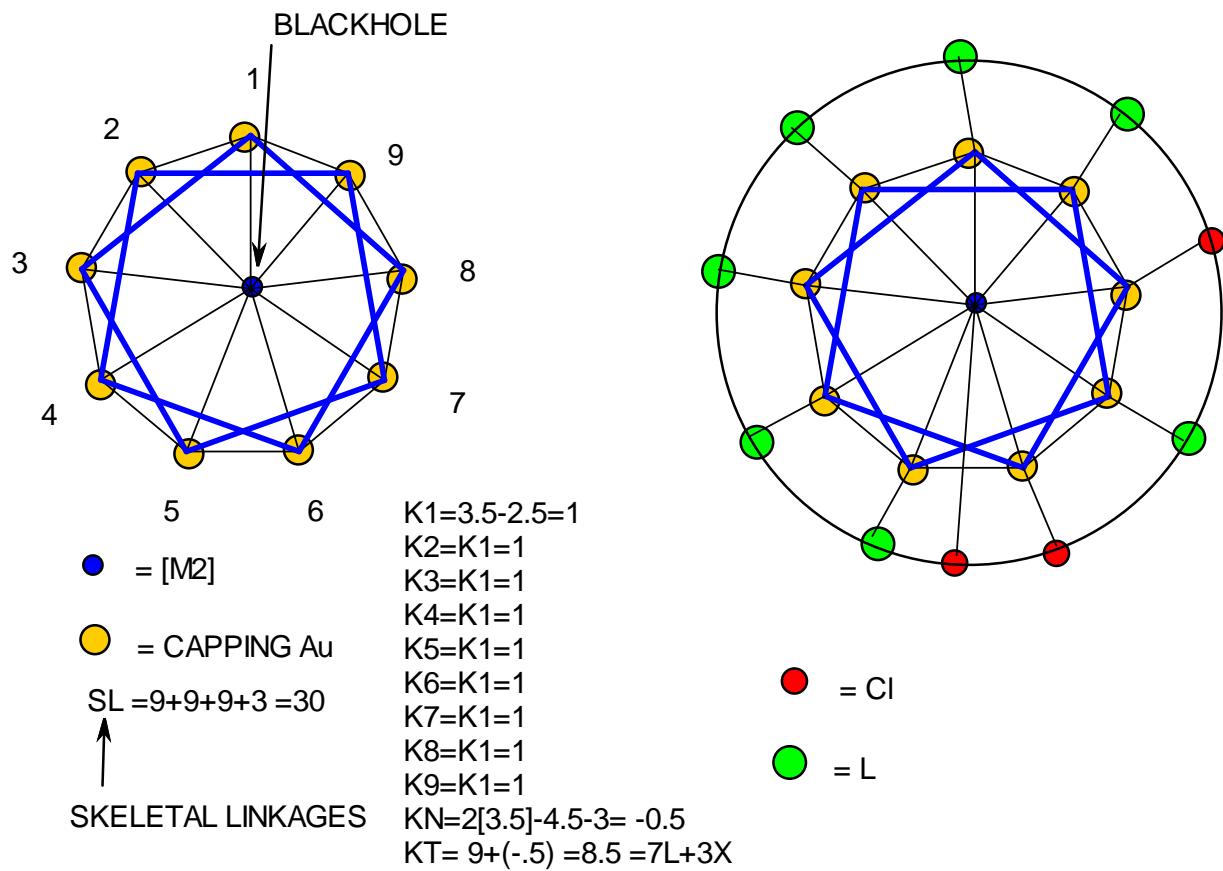
$V_e = 14n-16 = 14(11)-16 = 138$, $VF = 11[11]+14+3 = 138$; $K[M2] = 3$



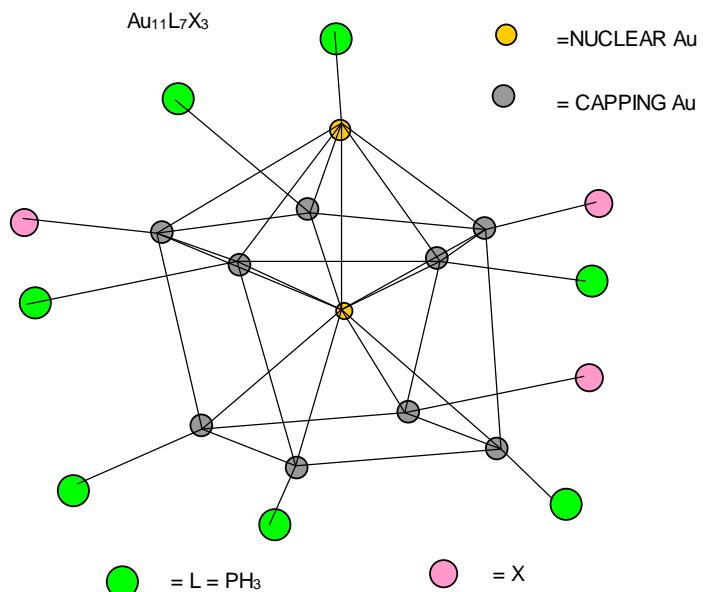
$K(n) = 30(11)$ belongs to $[M2]$ series.

$\text{Au}_{11}\text{L}_7\text{X}_3$: $K = 11[3.5]-7-1.5 = 30$, $K(n) = 30(11)$, $S = 4n-16$, $K_p = C^9C[M2]$

$V_e = 14n-16 = 14(11)-16 = 138$, $VF = 11[11]+14+3 = 138$; $K[M2] = 3$



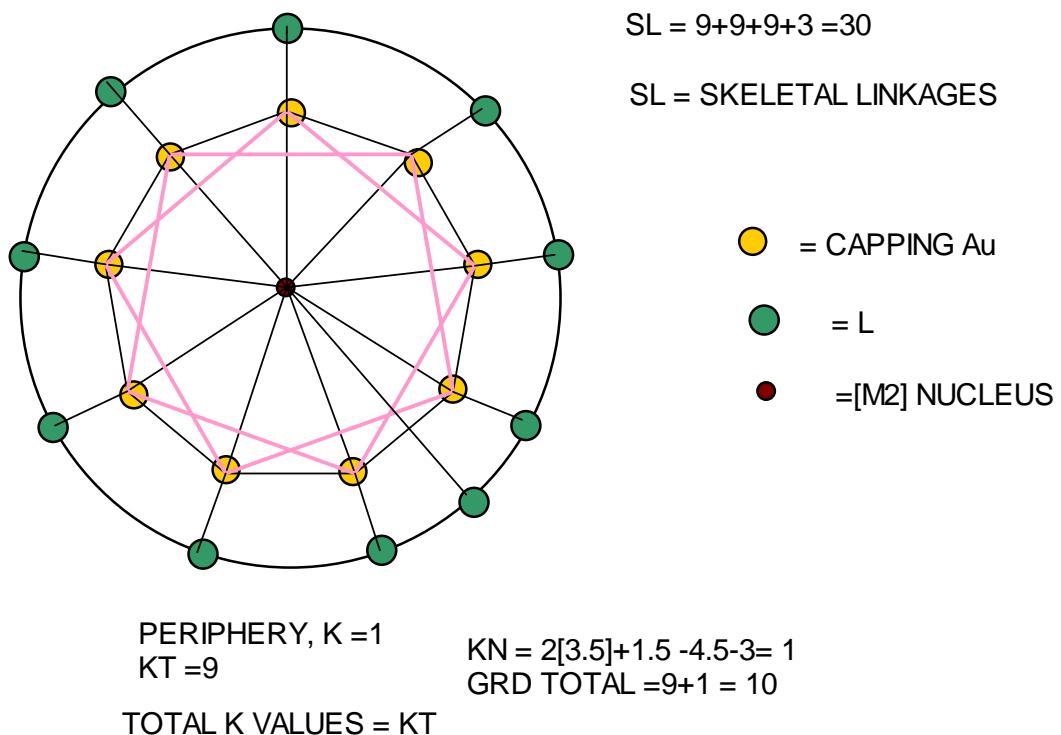
ISOMERISM



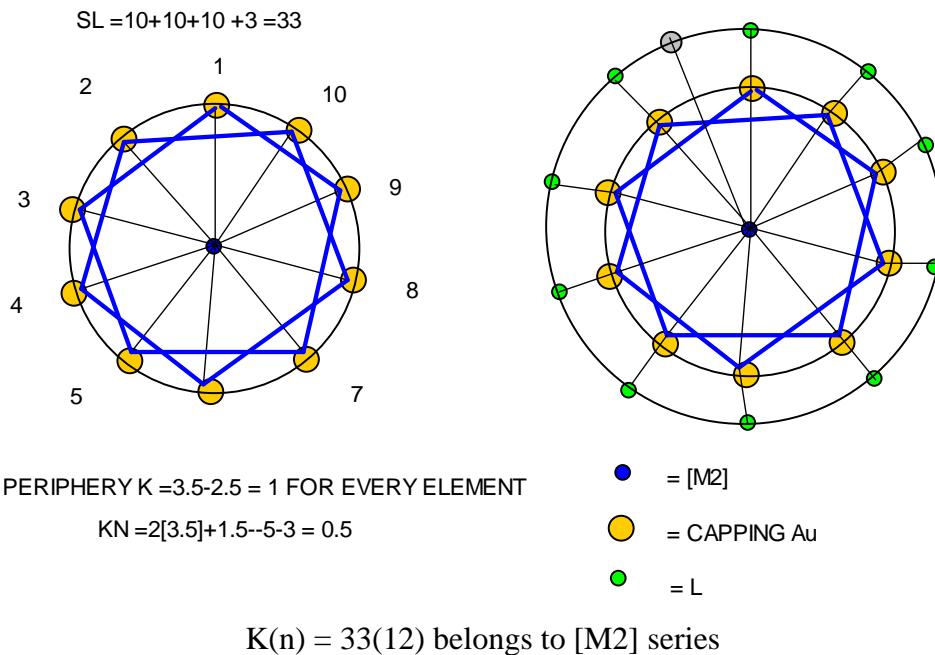
SKETCH OF THE OBSERVED STRUCTURE

$$\text{Au}_{11}\text{L}_{10}^{3+}: K = 11[3.5] - 10 + 1.5 = 30; K(n) = 30(11), S = 4n - 16, K_p = \text{C}^9\text{C}[\text{M}2]$$

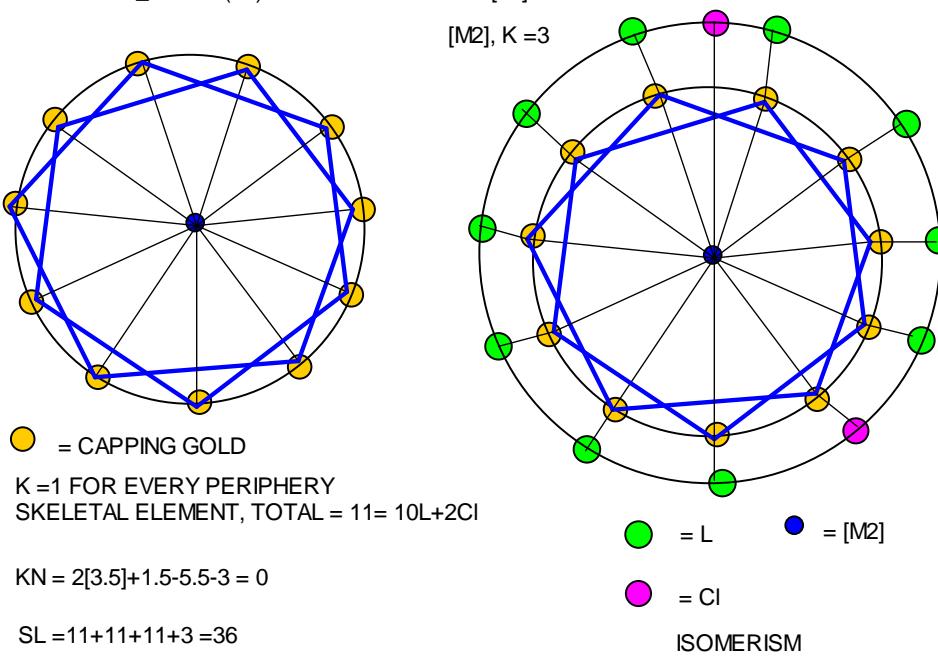
$$V_e = 14n - 16 = 14(11) - 16 = 138; V_F = 11[11] + 20 - 3 = 138$$



$\text{Au}_{12}\text{L}_{10}\text{Cl}^{3+}$: $K = 12[3.5]-10-0.5+1.5 = 33$; $K(n) = 33(12)$, $S = 4n-18$, $K_p = C^{10}\text{C}[\text{M}2]$
 $V_e = 14n-18 = 14(12)-18 = 150$; $VF = 12[11]+20+1-3 = 150$
 $[\text{M}2], K = 3$



$\text{Au}_{13}\text{L}_{10}\text{Cl}_2^{3+}$: $K = 13[3.5]-10-1+1.5 = 36$; $K(n) = 36(13)$, $S = 4n-20$, $K_p = C^{11}\text{C}[\text{M}2]$
 $V_e = 14n-20 = 14(13)-20 = 162$ $VF = 13[11]+20+2-3 =$

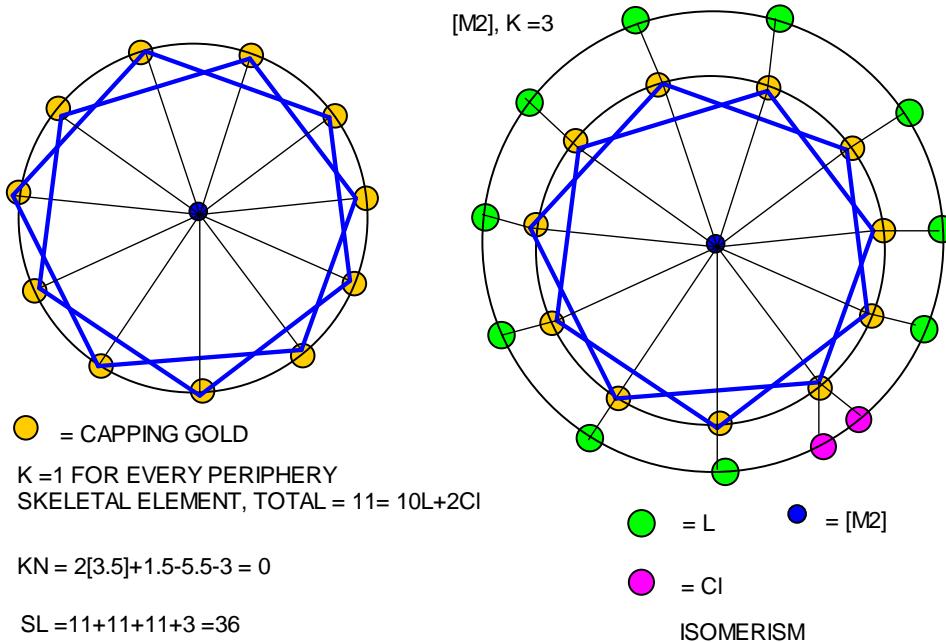


$K(n) = 36(13)$ belongs to $[\text{M}2]$ series.

$\text{Au}_{13}\text{L}_{10}\text{Cl}_2^{3+}$: $K = 13[3.5] - 10 - 1 + 1.5 = 36$; $K(n) = 36(13)$, $S = 4n - 20$, $K_p = \text{C}^{11}\text{C}[\text{M}2]$

$V_e = 14n - 20 = 14(13) - 20 = 162$

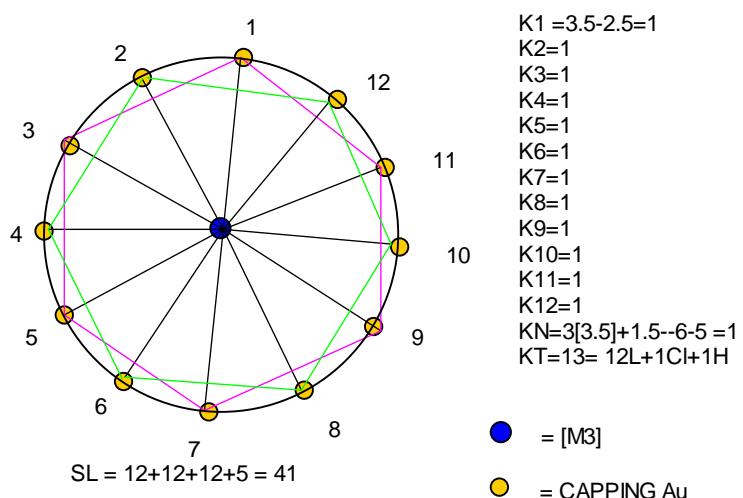
$V_F = 13[11] + 20 + 2 - 3 =$



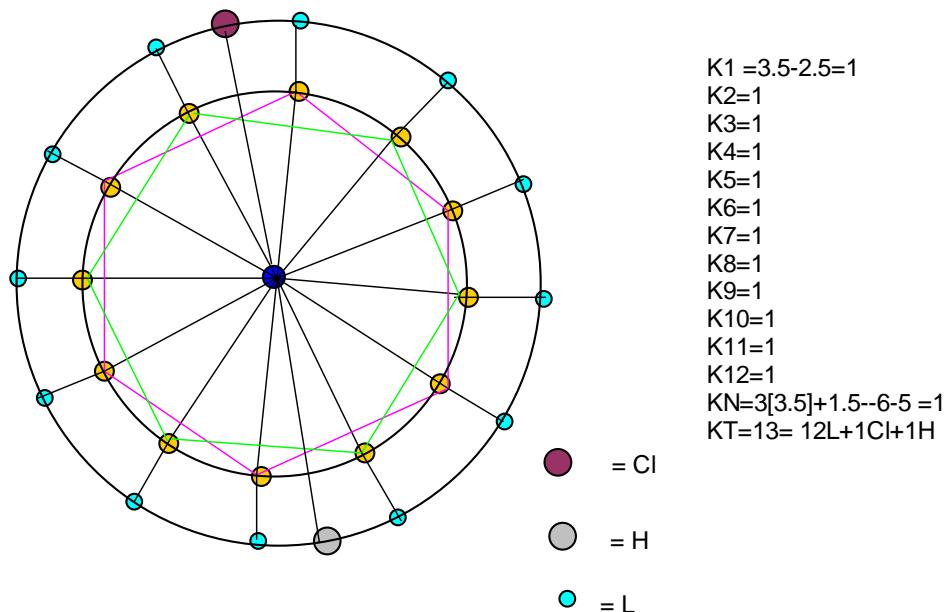
$\text{Au}_{15}\text{L}_{12}(\text{Cl})(\text{H})^{3+}$: $K = 15[3.5] - 12 - 1 + 1.5 = 41$; $K(n) = 41(15)$, $S = 4n - 22$, $K_p = \text{C}^{12}\text{C}[\text{M}3]$

$V_e = 14n - 22 = 14(15) - 22 = 188$; $V_F = 15[11] + 24 + 2 - 3 = 188$

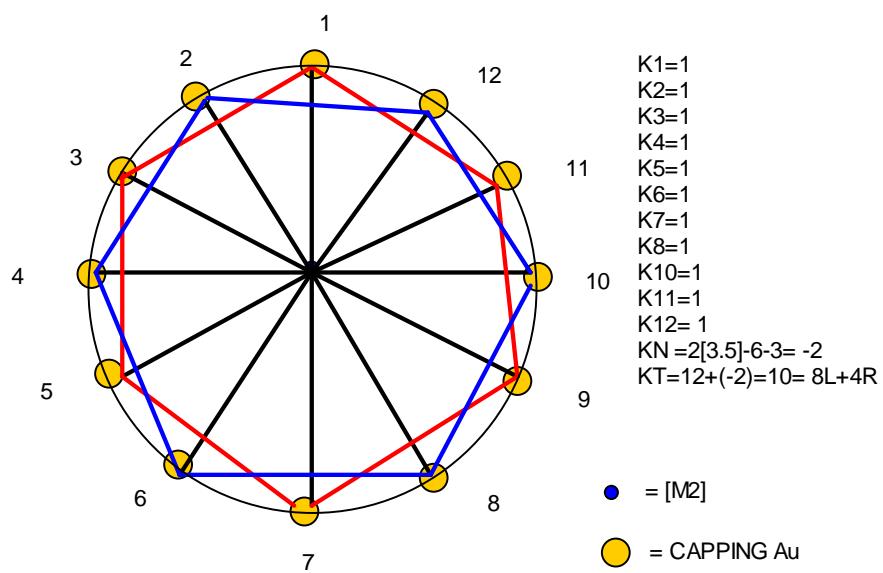
[M3], $K = 2n - 1 = 2(3) - 1 = 5$



$K(n) = 41(15)$ belongs to [M3] series.

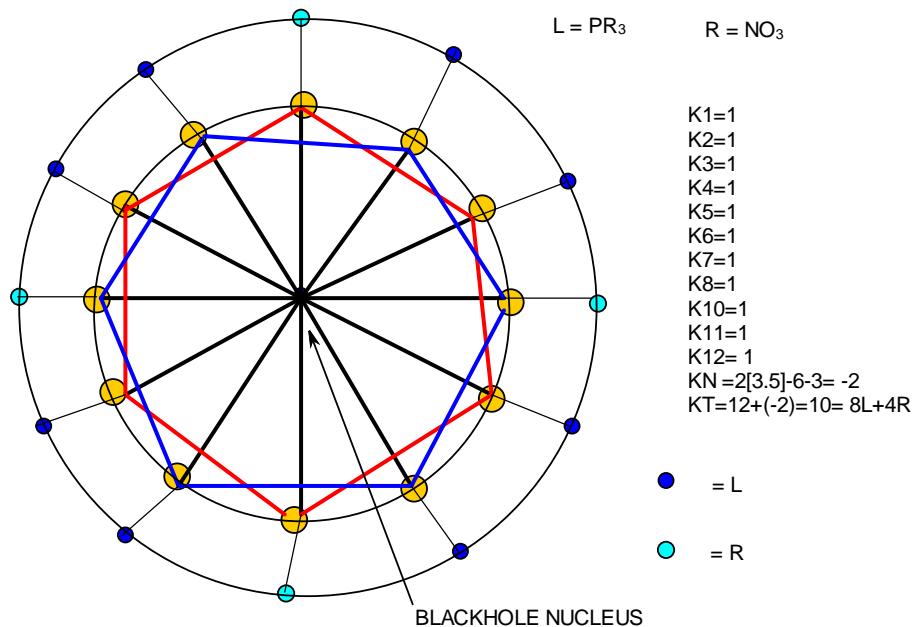


$Au_{14}L_8R_4$: $K = 14[3.5] - 8 - 2 = 39$, $K(n) = 39(14)$, $S = 4n - 22$, $K_p = C^{12}C[M2]$
 $\forall e = 14n - 22 = 14(14) - 22 = 174$; $\forall F = 14[11] + 16 + 4 = 174$ [M2], $K = 3$



$K(n) = 39(14)$ belongs to [M2] series.

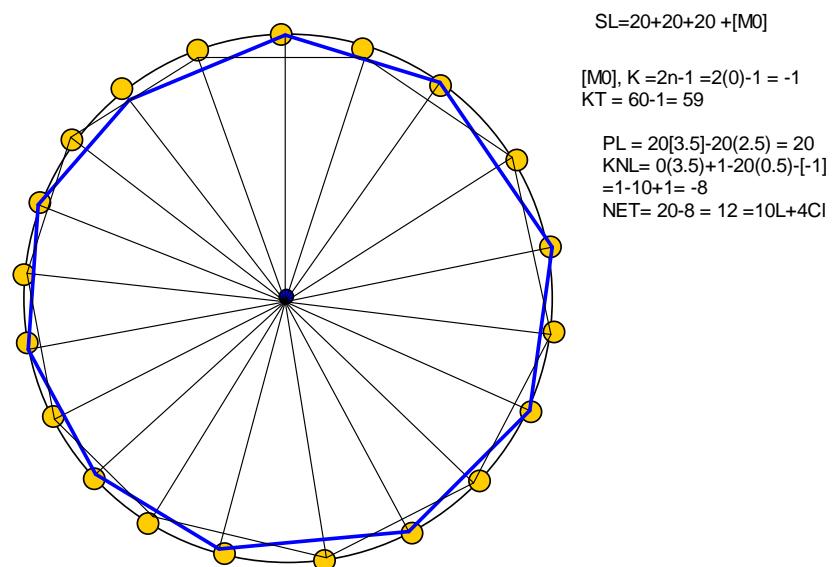
$\text{Au}_{14}\text{L}_8\text{R}_4$: $K = 14[3.5]-8-2 = 39$, $K(n) = 39(14)$, $S = 4n-22$, $K_p = \text{C}^{12}\text{C}[\text{M}2]$

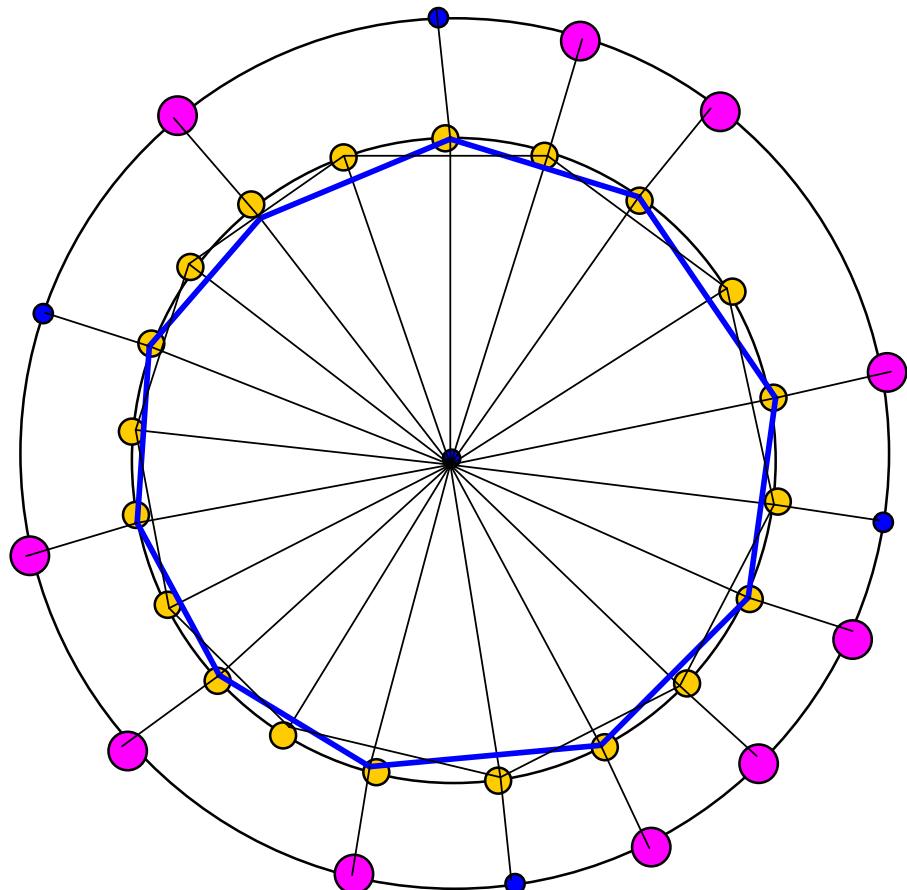


$K(n) = 59(20)$ belongs to $[\text{M}0]$ series.

$\text{Au}_{20}\text{L}_{10}\text{Cl}_4^{2+}$: $K = 20[3.5]-10-2+1 = 59$, $K(n) = 59(20)$, $S = 4n-38$, $K_p = \text{C}^{20}\text{C}[\text{M}0]$

$V_e = 14n-38 = 14(20)-38 = 242$, $VF = 20[11]+20+4-2 = 242$

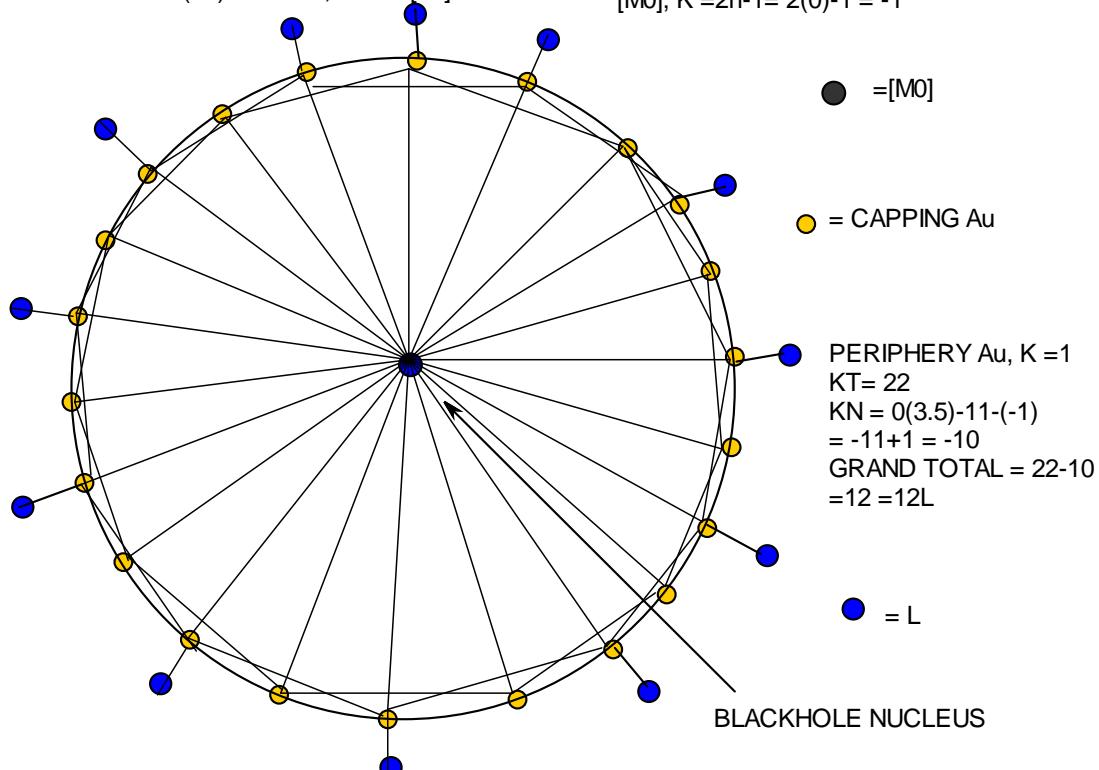


$$\text{Au}_{20}\text{L}_{10}\text{Cl}_4^{2+}: K = 20[3.5]-10-2+1 = 59, K(n) = 59(20), S = 4n-38, K_p = C^{20}C[M_0]$$
$$V_e = 14n-38 = 14(20)-38 = 242, V_F = 20[11]+20+4-2 = 242$$


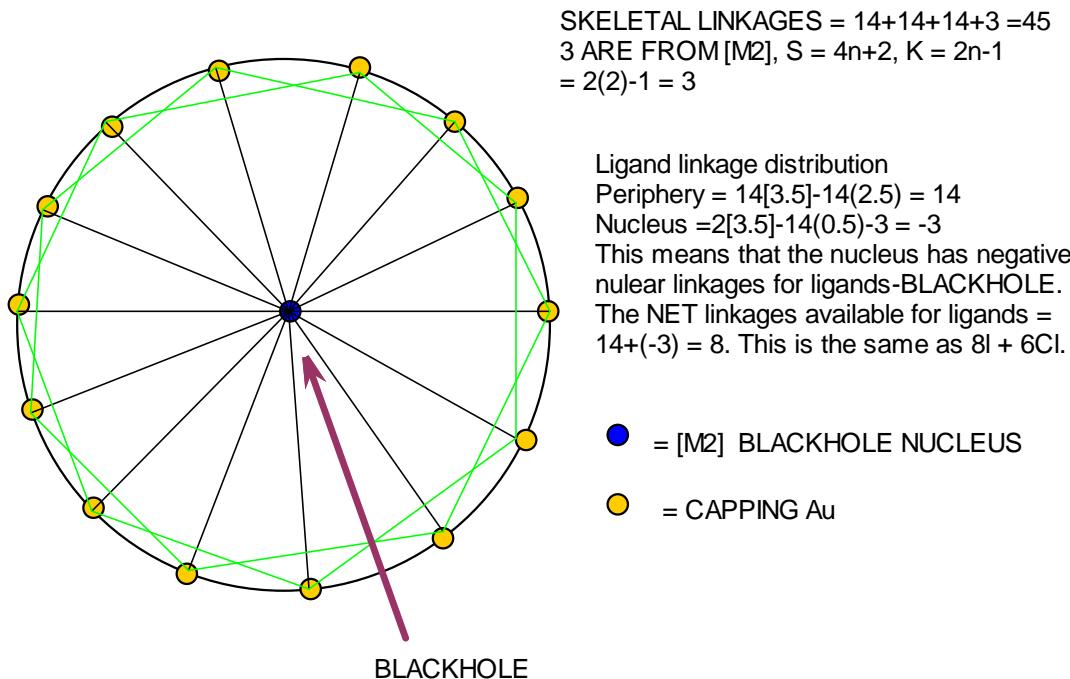
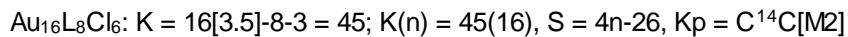
$\text{Au}_{22}\text{L}_{12}$: $K = 22[3.5]-12=65$; $K(n) = 65(22)$, $S = 4n-42$, $K_p = \text{C}^{22}\text{C}[\text{M}0]$

$V_e = 14n-42 = 14(22)-42 = 266$; $VF = 22[11]+24 = 266$

$[\text{M}0]$, $K = 2n-1 = 2(0)-1 = -1$



$K(n) = 65(22)$ belongs to $[\text{M}0]$ series.



$K(n) = 45(16)$ belongs to [M2] series.

The categorization of $K(n)$ values of the golden clusters into respective [Mx] clan groups can easily be verified using the appropriate series given in SRS-1. The calculation of K values and respective valence electrons from the series formula, Ve and the cluster formula, VF are given in Table 1. The clusters were regrouped according to [Mx] series and are presented in Table 2. In order to emphasize the idea of grouping the clusters according to [Mx] series, cluster group trees of selected clusters were constructed F-35 to F-37 for selected clusters of [M1], [M2] and [M6]. A proposed scheme for broad grouping of clusters is shown GR-1.

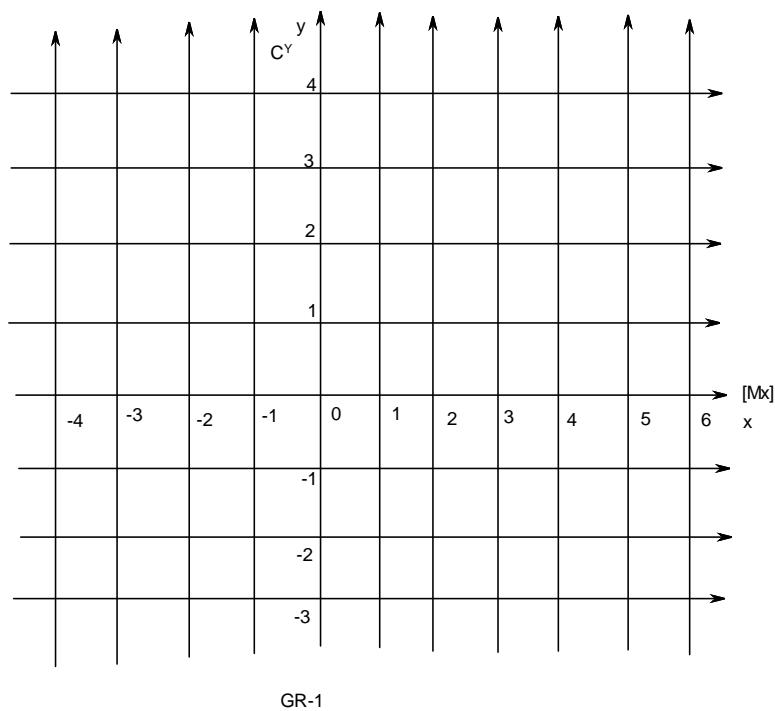
Table 1. Deducing $K(n)$ Parameter and Deriving the Series of Golden Clusters

| CLUSTER | n | K VALUE | K(n) | SERIES $S = 4n+q$ | $K_p = C^qC[Mx]$ | Ve $Ve = 14n+q$ | VF |
|---|----|--------------------------|--------|----------------------|------------------|--------------------|-------------------------|
| $\text{Au}_4\text{I}_2\text{L}_4$ | 4 | $4[3.5]-1-4 = 9$ | 9(4) | 4n-2 | $C^2C[M2]$ | $14(4)-2=54$ | $4[11]+2+8 = 54$ |
| $\text{Au}_6\text{L}_8^{2+}$ | 6 | $6[3.5]-8+1 = 14$ | 14(6) | 4n-4 | $C^3C[M3]$ | $14(6)-4=80$ | $6[11]+8(2)-2=80$ |
| $\text{Au}_6\text{L}_6^{2+}$ | 6 | $6[3.5]-6+1 = 16$ | 16(6) | 4n-8 | $C^5C[M1]$ | $14(6)-8=76$ | $6[11]+6(2)-2=76$ |
| $\text{Au}_7\text{L}_7^{+1}$ | 7 | $7[3.5]-7+0.5 = 18$ | 18(7) | 4n-8 | $C^5C[M2]$ | $14(7)-8=90$ | $7[11]+14-1=90$ |
| $\text{Au}_8\text{L}_8\text{Cl}_2^{2+}$ | 8 | $8[3.5]-8-1+1 = 20$ | 20(8) | 4n-8 | $C^5C[M3]$ | $14(8)-8=104$ | $8[11]+8(2)+2-2=104$ |
| $\text{Au}_8\text{L}_8^{2+}$ | 8 | $8[3.5]-8+1 = 21$ | 21(8) | 4n-10 | $C^6C[M2]$ | $14(8)-10=102$ | $8[11]+8(2)-2=102$ |
| $\text{Au}_8\text{L}_8^{2+}$ | 8 | $8[3.5]-7+1 = 22$ | 22(8) | 4n-12 | $C^7C[M1]$ | $14(8)-12=100$ | $8[11]+7(2)-2=100$ |
| $\text{Au}_9\text{L}_8^{+}$ | 9 | $9[3.5]-8+0.5 = 24$ | 24(9) | 4n-12 | $C^7C[M2]$ | $14(9)-12=114$ | $9[11]+16-1 = 114$ |
| $\text{Au}_9\text{L}_8^{3+}$ | 9 | $9[3.5]-8+1.5 = 25$ | 25(9) | 4n-14 | $C^8C[M1]$ | $14(9)-14=112$ | $9[11]+8(2)-3=112$ |
| L=PAR3 | | | | | | | |
| $\text{Au}_{10}\text{L}_8\text{Cl}^{+}$ | 10 | $10[3.5]-8-0.5+0.5 = 27$ | 27(10) | 4n-14 | $C^8C[M2]$ | $14(10)-14=126$ | $10[11]+16+1-1=126$ |
| $\text{Au}_{10}\text{L}_6\text{Cl}_3^{+}$ | 10 | $10[3.5]-6-1.5+0.5 = 28$ | 28(10) | 4n-16 | $C^9C[M1]$ | $14(10)-16=124$ | $10[11]+6(2)+3-1 = 124$ |
| $\text{Au}_{10}\text{L}_3\text{R}_4$ | 10 | $10[3.5]-3-2 = 30$ | 30(10) | 4n-20 | $C^{11}C[M-1]$ | $14(10)-20=120$ | $10[11]+3(2)+4 = 120$ |
| $\text{Au}_{11}\text{L}_{12}^{3+}$ | 11 | $11[3.5]-12+1.5 = 28$ | 28(11) | 4n-12 | $C^7C[M4]$ | $14(11)-12=142$ | $11[11]+12(2)-3 = 142$ |
| $\text{Au}_{11}\text{L}_8\text{Cl}_3$ | 11 | $11[3.5]-8-1.5 = 29$ | 29(11) | 4n-14 | $C^8C[M3]$ | $14(11)-14=140$ | $11[11]+8(2)+3 = 140$ |
| $\text{Au}_{11}\text{L}_7\text{X}_3$ | 11 | $11[3.5]-7-1.5 = 30$ | 30(11) | 4n-16 | $C^9C[M2]$ | $14(11)-16=138$ | $11[11]+7(2)+3 = 138$ |
| L=PAR3 X= Cl | | | | | | | |
| $\text{Au}_{11}\text{L}_8\text{Cl}_2^{+}$ | 11 | $11[3.5]-8-1+0.5 = 30$ | 30(11) | 4n-16 | $C^9C[M2]$ | $14(11)-16=138$ | $11[11]+8(2)+2-1=138$ |

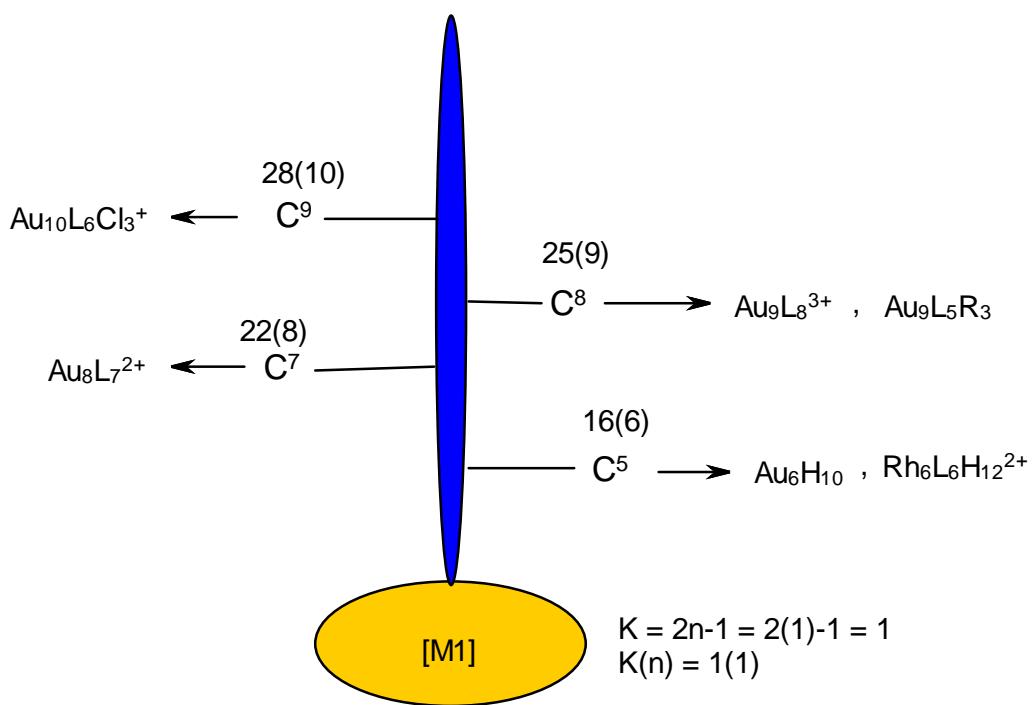
| | | | | | | | |
|--|-----|---------------------------|----------|--------|--------------------------|------------------|----------------------|
| Au ₁ L ₁₀ ³⁺ | 11 | 11[3.5]-10+1.5=30 | 30(11) | 4n-16 | C ⁹ C[M2] | 14(11)-16=138 | 11[11]+10(2)-3=138 |
| Au ₁₂ L ₁₀ Cl ³⁺ | 12 | 12[3.5]-10-0.5+1.5=33 | 33(12) | 4n-18 | C ¹⁰ C[M2] | 14(12)-18=150 | 12[11]+20+1-3=150 |
| Au ₁₃ L ₁₀ Cl ₂ ³⁺ | 13 | 13[3.5]-10-1+1.5=36 | 36(13) | 4n-20 | C ¹¹ C[M2] | 14(13)-20=162 | 13[11]+10(2)+2-3=162 |
| Au ₁₃ L ₈ Cl ₄ ⁺ | 13 | 13[3.5]-8-2+0.5=36 | 36(13) | 4n-20 | C ¹¹ C[M2] | 14(13)-20=162 | 13[11]+10(2)+2-3=162 |
| Au ₁₅ L ₁₂ Cl(H) ³⁺ | 15 | 15[3.5]-12-0.5-0.5+1.5=41 | 41(15) | 4n-22 | C ¹² C[M3] | 14(15)-22=188 | 15[11]+24+2-3=188 |
| Au ₁₆ L ₈ X ₈ | 16 | 16[3.5]-8-4=44 | 44(16) | 4n-24 | C ¹³ C[M3] | 14(16)-24=200 | 16[11]+16+8=200 |
| Au ₂₀ L ₁₀ Cl ₄ ²⁺ | 20 | 20[3.5]-10-2+1=59 | 59(20) | 4n-38 | C ²⁰ C[M0] | 14(20)-38=242 | 20[11]+10(2)+4-2=242 |
| Au ₂₂ L ₁₂ | 22 | 22[3.5]-12=65 | 65(22) | 4n-42 | C ²² C[M0] | 14(22)-42=266 | 22[11]+12(2)=266 |
| Au ₂₄ L ₁₀ R ₅ X ₂ ⁺¹ | 24 | 24[3.5]-10-2.5-1+0.5=71 | 71(24) | 4n-46 | C ²⁴ C[M0] | 14(24)-46=290 | 24[11]+20+5+2-1=290 |
| Au ₂₅ L ₁₀ (SR) ₅ ²⁺ | 25 | 25[3.5]-10-2.5+1=76 | 76(25) | 4n-52 | C ²⁷ C[M-2] | 14(25)-52=298 | 25[11]+10(2)+5-2=298 |
| Au ₃₆ R ₃₄ | 36 | 36[3.5]-17=109 | 109(36) | 4n-74 | C ³⁸ C[M-2] | 14(36)-74=430 | 36[11]+34=430 |
| Au ₃₈ L ₁₈ Cl ₂ ⁴⁺ | 38 | 38[3.5]-18-1+2=116 | 116(38) | 4n-80 | C ⁴¹ C[M-3] | 14(38)-80=452 | 38[11]+36+2-4=452 |
| Au ₃₉ L ₁₄ Cl ₆ ³⁺ | 39 | 39[3.5]-14-3+1.5=121 | 121(39) | 4n-86 | C ⁴⁴ C[M-5] | 14(39)-86=460 | 39[11]+28+6-3=460 |
| Au ₃₉ L ₁₄ Cl ₆ ⁺¹ | 39 | 39[3.5]-14-3+0.5=120 | 120(39) | 4n-84 | C ⁴³ C[M-4] | 14(39)-84=462 | 39[11]+28+6-1=462 |
| Au ₄₀ R ₂₄ | 40 | 40[3.5]-12=128 | 128(40) | 4n-96 | C ⁴⁹ C[M-9] | 14(40)-96=464 | 40[11]+24=464 |
| Au ₁₀₂ R ₄₄ | 102 | 102[3.5]-22=335 | 335(102) | 4n-262 | C ¹³² C[M-30] | 14(102)-262=1166 | 102[11]+44=1166 |

Table 2. Grouping of Golden Clusters

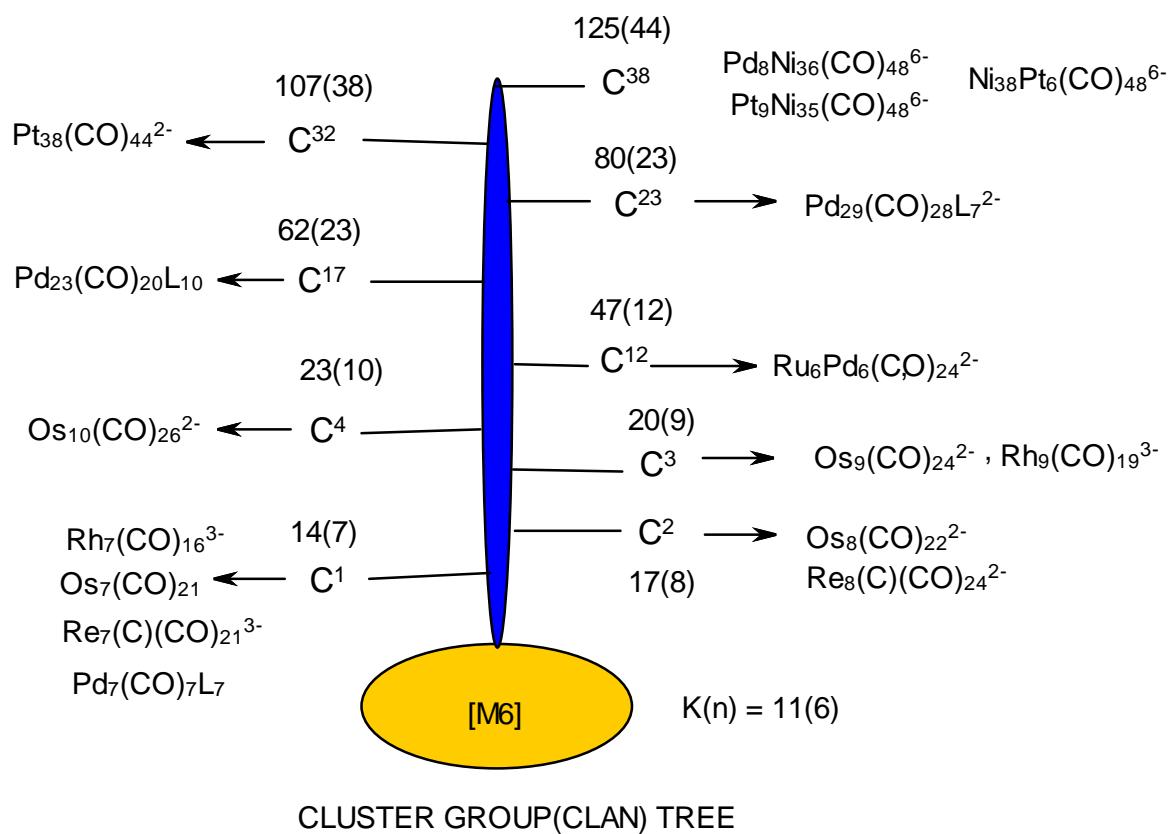
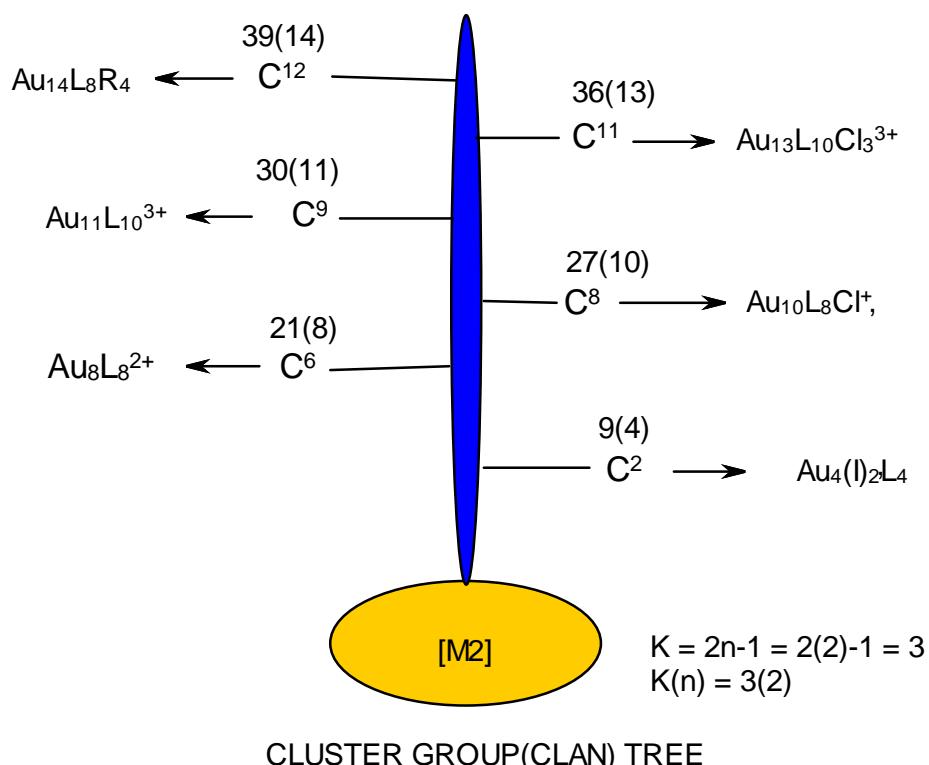
| CLUSTER | K(n) | Kp = C ^y C[Mx] | CLOSOS SERIES, [Mx] | CLAN | GROUP | BLACK HOLES |
|--|----------|---------------------------|------------------------|--------|-------|-------------------|
| | | y | X value | | | |
| Au ₁₄₄ R ₆₀ | 474(144) | 187 | -43 | [M-43] | | BLACKHOLE NUCLEUS |
| Au ₁₀₂ R ₄₄ | 335(102) | 132 | -30 | [M-30] | | BLACKHOLE NUCLEUS |
| Au ₄₀ R ₂₄ | 128(40) | 49 | -9 | [M-9] | | BLACKHOLE NUCLEUS |
| Au ₃₉ L ₁₄ Cl ₆ ³⁺ | 121(39) | 44 | -5 | [M-5] | | BLACKHOLE NUCLEUS |
| Au ₃₉ L ₁₄ Cl ₆ ⁺¹ | 120(39) | 43 | -4 | [M-4] | | BLACKHOLE NUCLEUS |
| Au ₃₈ L ₁₈ Cl ₂ ⁴⁺ | 116(38) | 41 | -3 | [M-3] | | BLACKHOLE NUCLEUS |
| Au ₃₆ R ₃₄ | 109(36) | 38 | -2 | [M-2] | | BLACKHOLE NUCLEUS |
| Au ₂₅ L ₁₀ (SR) ₅ ²⁺ | 76(25) | 27 | -2 | [M-2] | | BLACKHOLE NUCLEUS |
| Au ₁₀ L ₃ R ₄ | 30(10) | 11 | -1 | [M-1] | | BLACKHOLE NUCLEUS |
| Au ₂₀ L ₁₀ Cl ₄ ²⁺ | 59(10) | 20 | 0 | [M0] | | BLACKHOLE NUCLEUS |
| Au ₂₂ L ₁₂ | 65(22) | 22 | 0 | [M0] | | BLACKHOLE NUCLEUS |
| Au ₆ H ₁₀ | 16(6) | 5 | 1 | [M1] | | |
| Rh ₆ L ₆ H ₁₂ ²⁺ | 16(6) | 5 | 1 | [M1] | | |
| Au ₈ L ₇ ⁺² | 22(8) | 7 | 1 | [M1] | | |
| Au ₉ L ₈ ⁺³ | 25(9) | 8 | 1 | [M1] | | |
| Au ₁₀ L ₆ Cl ₃ ⁺¹ | 28(10) | 9 | 1 | [M1] | | |
| Au ₄ L ₄ ₂ | 9(4) | 2 | 2 | [M2] | | |
| Au ₈ L ₈ ⁺² | 21(8) | 6 | 2 | [M2] | | |
| Au ₁₀ L ₈ Cl ⁺¹ | 27(10) | 8 | 2 | [M2] | | |
| Au ₁₁ L ₁₀ ³⁺ | 30(11) | 9 | 2 | [M2] | | |
| Au ₁₁ L ₇ X ₃ | 30(11) | 9 | 2 | [M2] | | |
| Au ₁₂ L ₁₀ Cl ₃ ³⁺ | 33(12) | 10 | 2 | [M2] | | |
| Au ₁₃ L ₁₀ Cl ₃ ³⁺ | 36(13) | 11 | 2 | [M2] | | |
| Au ₁₄ L ₈ R ₄ | 39(14) | 12 | 2 | [M2] | | |
| Au ₆ L ₈ ⁺² | 14(6) | 3 | 3 | [M3] | | |
| Au ₆ L ₈ ⁺² | 14(6) | 3 | 3 | [M3] | | |
| Au ₈ L ₈ Cl ₂ ²⁺ | 20(8) | 5 | 3 | [M3] | | |
| Au ₁₅ L ₁₂ (Cl)(H) ³⁺ | 41(15) | 12 | 3 | [M3] | | |
| Zn ₆ H ₁₀ | 13(6) | 2 | 4 | [M4] | | |
| B ₅ H ₉ | 8(5) | -1 | 6 | [M6] | | |
| B ₄ H ₁₀ | 5(4) | -2 | 6 | [M6] | | |
| B ₅ H ₁₀ | 10(6) | -1 | 7 | [M7] | | |
| C ₆ H ₁₀ | 7(6) | -4 | 10 | [M10] | | |



Clan (Group) Cluster Trees

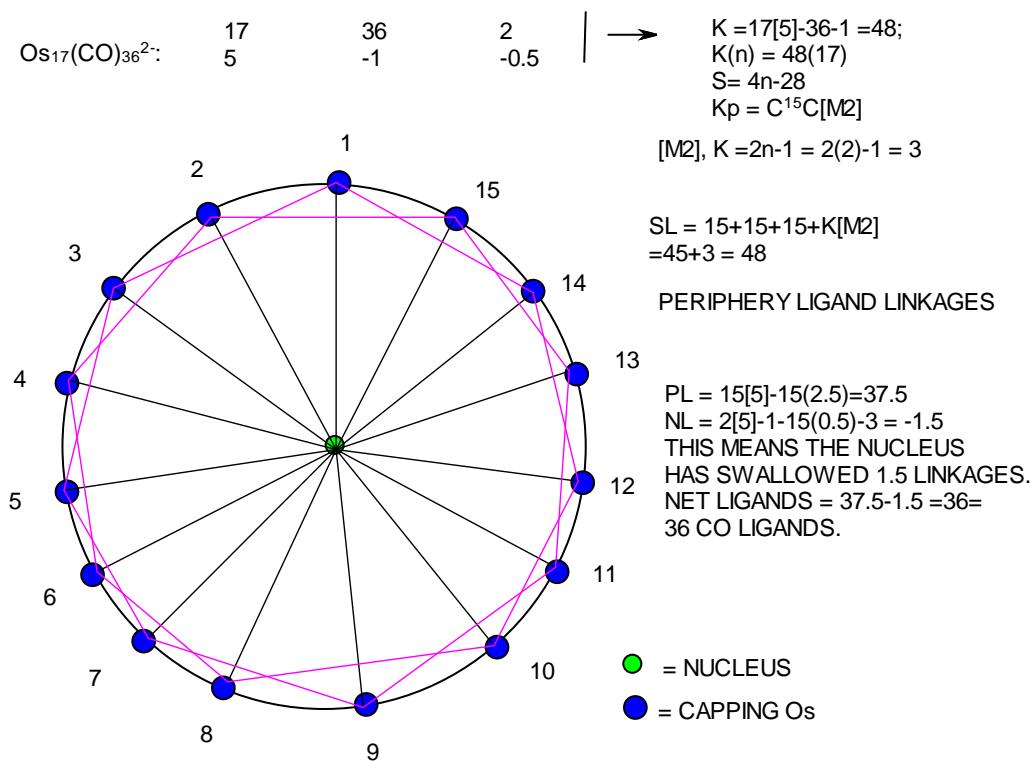


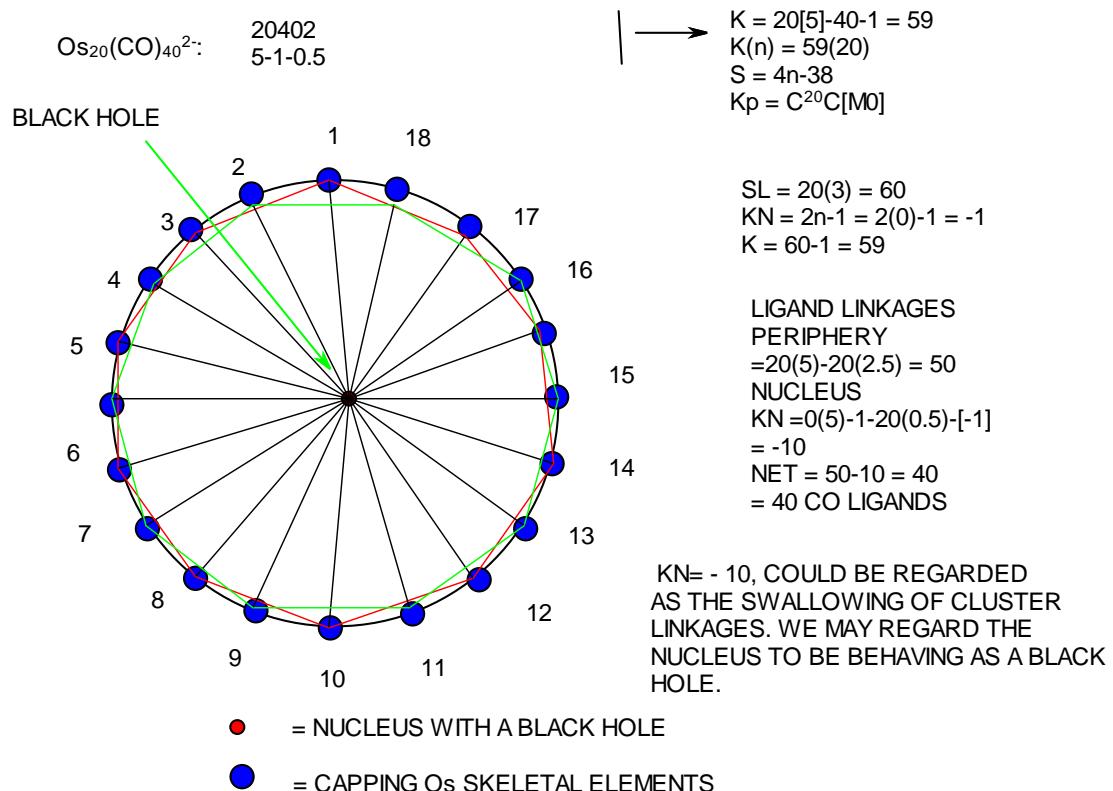
CLUSTER GROUP(CLAN) TREE



The Existance of Blackholes in the Nuclei of Some Golden Clusters

In the previous work, it was discovered that the series method could be applied to the analysis and categorization of golden clusters (Kiremire, 2016a 2017a). It was also found that the majority of the simple clusters of nuclearity index 4-13 had either ONE or TWO golden skeletal elements in the cluster nucleus (Kiremire, 2016a, 2017a). This information was in agreement with earlier observation by the series method that indeed some clusters had octahedral cluster nuclei in them (Kiremire, 2016b). The subsequent work also revealed that, clusters could be explained more clearly in terms of their structures and ligand distribution onto skeletal elements by using skeletal numbers and valences (Kiremire, 2017c). Using skeletal numbers and the ligand distribution concept, it has been discovered that some golden cluster nuclei with $[Mx]$, where $x \leq 0$ do “swallow” skeletal and/or ligand linkages. As a consequence, the numbers of linkages left for binding to ligands are considerably diminished giving rise to some golden clusters being left naked, that is, having no ligands at all. It is proposed that clusters with nuclei which appear to “swallow” cluster linkages be regarded as NUCLEI WITH BLACKHOLES. Examples of golden clusters having nuclei with black-holes are given F-38 to F-41.

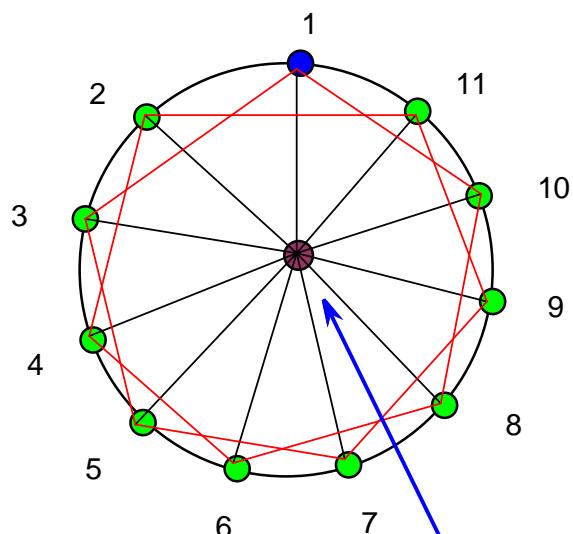




$\text{Au}_{10}\text{L}_3\text{R}_4:$

| | | |
|-----|----|------|
| 10 | 3 | 4 |
| 3.5 | -1 | -0.5 |

- = CAPPING Au
- = [M-1] NUCLEUS
- = FICTITIOUS ELEMENT



$$\begin{aligned} \text{SL} &= 11 + 11 + 11 + K[M-1] \\ &= 33 - 3 = 30 \end{aligned}$$

| →

$K = 10[3.5] - 3 - 2 = 30$
 $K(n) = 30(10)$
 $S = 4n - 20$
 $K_p = C^{11}\text{C}[M-1]$
 THUS, 11 SKELETAL ELEMENTS
 CAPPING ONE OF WHICH IS
 FICTITIOUS(EMPTY HOLE) SINCE
 WE HAVE ONLY 10 AVAILABLE
 SKELETAL ELEMENTS.

$$[M-1], K = 2n - 1 = 2(-1) - 1 = -3$$

THIS MEANS THREE SKELETAL LINKAGES HAVE BEEN SWALLOWED.

PERIPHERY LIGAND LINKAGES
 $PL = 11[3.5] - 11(2.5) = 11$
 NUCLEAR LIGAND LINKAGES
 $= -1[3.5] - 11(0.5) - [-3] = -6$
 THUS, SIX LIGAND LINKAGES HAVE BEEN
 SWALLOWED BY THE NUCLEUS.
 NET = $11 - 6 = 5 = 3L + 4R$

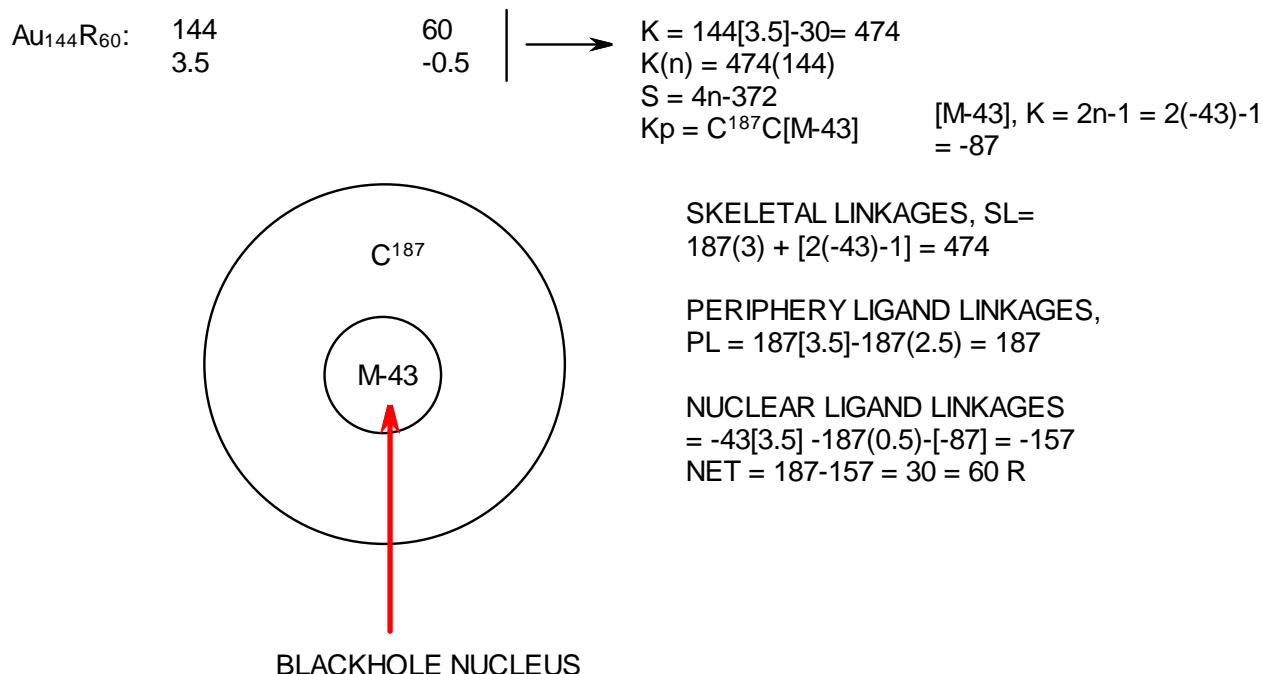


Table 3. Data Interpretation

| | | K | K(n) | SERIES | K _p | V _e | VF | RESULT |
|----|---|-------------------------|--------|--------|------------------------------|-------------------|---------------------|-----------|
| 1 | $\text{Au}_6\text{L}_8^{2+}$ | $6[3.5]-8+1 = 14$ | 14(6) | 4n-4 | $\text{C}^3\text{C}[M3]$ | $14(6)-4=80$ | $6[11]+16-2=80$ | Different |
| 2 | $\text{Au}_7\text{L}_8^{3+}$ | $7[3.5]-8+1.5= 18$ | 18(7) | 4n-8 | $\text{C}^5\text{C}[M2]$ | $14(7)-8 = 90$ | $7[11]+16-3=90$ | Different |
| 3 | $\text{Au}_6\text{L}_8^{2+}$ | $6[3.5]-8+1 = 14$ | 14(6) | 4n-4 | $\text{C}^3\text{C}[M3]$ | $14(6)-4=80$ | $6[11]+16-2=80$ | Different |
| 4 | $\text{Au}_8\text{L}_8\text{Cl}_2^{2+}$ | $8[3.5]-8-1+1 = 20$ | 20(8) | 4n-8 | $\text{C}^5\text{C}[M3]$ | $14(8)-8=104$ | $8[11]+16+2-2=104$ | Different |
| 5 | $\text{Au}_{11}\text{L}_{12}^{3+}$ | $11[3.5]-12+1.5 = 28$ | 28(11) | 4n-12 | $\text{C}^7\text{C}[M4]$ | $14(11)-12=142$ | $11[11]+24-3 = 142$ | Different |
| 6 | $\text{Au}_{11}\text{L}_7\text{Cl}_3$ | $11[3.5]-7-1.5 = 30$ | 30(11) | 4n-16 | $\text{C}^9\text{C}[M2]$ | $14(11)-16=138$ | $11[11]+14+3 = 138$ | Similar |
| 7 | $\text{Au}_{11}\text{L}_8\text{Cl}_2^{+}$ | $11[3.5]-8-1+0.5 = 30$ | 30(11) | 4n-16 | $\text{C}^9\text{C}[M2]$ | 138 | $11[11]+16+2-1=138$ | Similar |
| 8 | $\text{Au}_{20}\text{L}_8^{4+}$ | $20[3.5]-8+2 = 64$ | 64(20) | 4n-48 | $\text{C}^{25}\text{C}[M-5]$ | $14(20)-48=232$ | $20[11]+16-4=232$ | Similar? |
| 9 | $\text{Au}_{13}\text{L}_{10}\text{Cl}_2^{3+}$ | $13[3.5]-10-1+1.5 = 36$ | 36(13) | 4n-20 | $\text{C}^{11}\text{C}[M2]$ | $14(13)-20=162$ | $13[11]+20+2-3=162$ | Similar? |
| 10 | $\text{Au}_{22}\text{L}_{12}$ | $22[3.5]-12 = 65$ | 65(22) | 4n-42 | $\text{C}^{22}\text{C}[M0]$ | $14(22)-42 = 266$ | $22[11]+24=266$ | Different |
| 11 | $\text{Au}_{22}\text{L}_{14}$ | $22[3.5]-14 = 63$ | 63(22) | 4n-38 | $\text{C}^{20}\text{C}[M2]$ | $14(22)-38 = 270$ | $22[11]+28=270$ | Different |

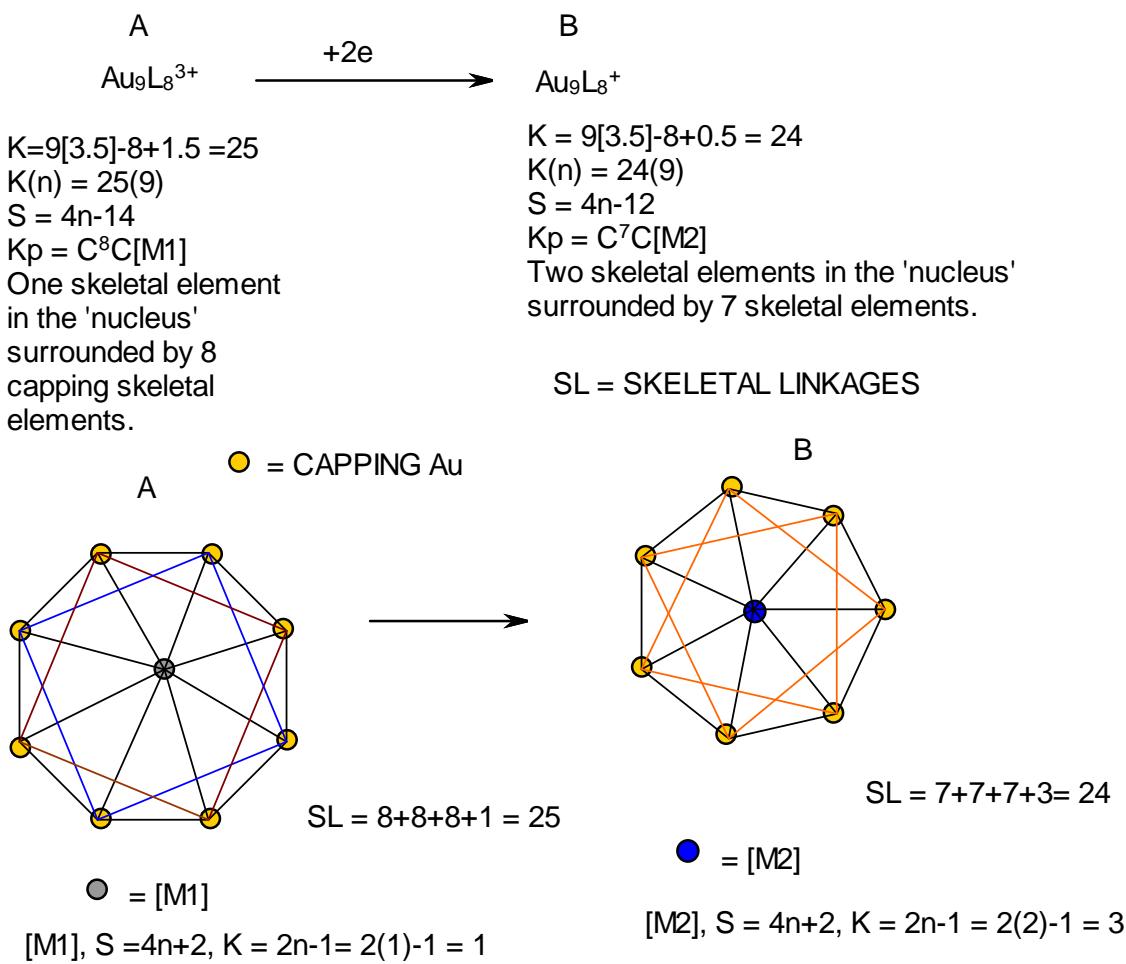
3. Data Interpretation

A number of golden clusters have been studied by UV-Vis-NID method (Wang, et al, 2016). For the purposes of illustrating how the series method analysis of clusters could be utilized, these findings are given in Table 3. For ease of differentiation of the clusters and grouping them, let us refer to the clusters with the same closo nucleus [Mx] as being in the same CLUSTER GROUP but different series $S = 4n+q$ (q varies), while those which belong to the same series $S = 4n+q$ (q is the same) as being in the same CLUSTER PERIOD. This approach is similar to what we have in the ordinary periodic table of elements. Let us look at the following clusters: $\text{Pd}_{10}(\text{CO})_{12}\text{L}_6$; $K(n) = 22(10)$, $S = 4n-4$, $K_p = \text{C}^3\text{C}[M7]$; $\text{Pd}_{23}(\text{CO})_{21}\text{L}_{10}$; $K = 61(23)$, $S = 4n-30$, $K_p = \text{C}^{16}\text{CM7}$ and $\text{Au}_4\text{Pd}_{28}(\text{CO})_{22}\text{L}_{16}$; $K=88(32)$, $S=4n-48$, $K_p = \text{C}^{25}\text{C}[M7]$. All these three clusters possess the similar cluster nucleus [M7] but different number of capping elements. These clusters are regarded as being in the same CLUSTER GROUP but different cluster capping periods-one has 3 capping skeletal elements, the other 16 capping elements and lastly the other has 25 capping elements. Let us take another example: $\text{Pd}_{29}(\text{CO})_{28}\text{L}_7^{2-}$: $\text{Pd}_{30}(\text{CO})_{26}\text{L}_{10}$; $K = 84$, $K(n) = 84(30)$, $S= 4n-48$, $K_p = \text{C}^{25}\text{C}[M5]$ and $\text{Au}_4\text{Pd}_{28}(\text{CO})_{22}\text{L}_{16}$; $K=88(32)$, $S=4n-48$, $K_p = \text{C}^{25}\text{C}[M7]$. These two clusters belong to the same CLUSTER PERIOD, $S = 4n-48$. They have the same number of capping elements but different nuclear sizes, one with 5 skeletal elements in the nucleus and the other 7. With this proposed definition of CLUSTER GROUP and CLUSTER PERIOD introduced, we

can now have some idea or understanding of the results indicated in the table. According to the series method, clusters 1 {[M3], C³} and 2 {[M2], C⁵}:-these two belong to different cluster groups and cluster periods;clusters 3 {[M3], C³}, 4 {[M3], C⁵}, and 5 {[M4], C⁷}:- cluster 3 and 4 belong to the same group but different periods while cluster 5 has nothing in common with clusters 3 and 4; 6 {[M2], C⁹} and 7 {[M2], C⁹}:-clusters 6 and 7 belong to the same group and period; 8 {[M-5], C²⁵}, 9 {[M2], C¹¹}:-clusters 8 and 9 have nothing in common; 10 {[M0], C²²} and 11 {[M2], C²⁰}:-clusters 10 and 11 are also different as they have nothing in common.

CONVERSION OF $\text{A}_9\text{L}_8^{3+}$ CLUSTER TO Au_9L_8^+ CLUSTER

The change of skeletal structure of $\text{A}_9\text{L}_8^{3+}$ to a different one of Au_9L_8^+ was reported by Mingos (Mingos, 1984). This transformation can also be explained by the series approach. The K(n) value of $\text{Au}_9\text{L}_8^{3+}$ is 25(9) while that of Au_9L_8^+ is 24(9). The decrease in K value by 1 results in a decrease of skeletal capping by 1 with a parallel increase in the nuclear index by 1. That is, instead of the geometry having 8 capping elements and 1 in the nucleus it changes into another one having 7 capping skeletal elements and 2 nuclear elements. In terms of cluster grouping proposed, the cluster has moved from CLUSTER GROUP 1[M1] to CLUSTER GROUP 2[M2]. This is illustrated in F-42.



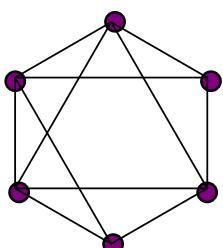
Cluster Isomerism

Skeletal elements with the same nuclearity index (n) and same skeletal number K have been found to portray different geometrical shapes. We can refer to this as K ISOMERISM. This has been observed (Hughes & Wade, 2000) for $\text{Os}_6(\text{CO})_{18}^{2-}$ [K = 11] and $\text{Os}_6(\text{H})_2(\text{CO})_{18}$ [K = 11] in F-43. The encounter with K isomerism in golden cluster $\text{A}_9\text{L}_8^{3+}$ (Mingos, 1984) is not a surprise. The rough sketches of the isomerism are illustrated in F-43 to F-48.

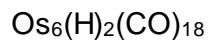
K- ISOMERISM



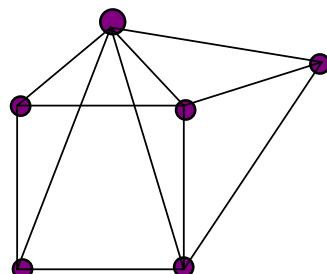
$$\begin{aligned} K &= 6[5]-18-1 = 11 \\ K(n) &= 11(6) \\ S &= 4n+2 \\ \text{CLOSO; } &[\text{M}6] \end{aligned}$$



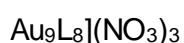
$$K = 11$$



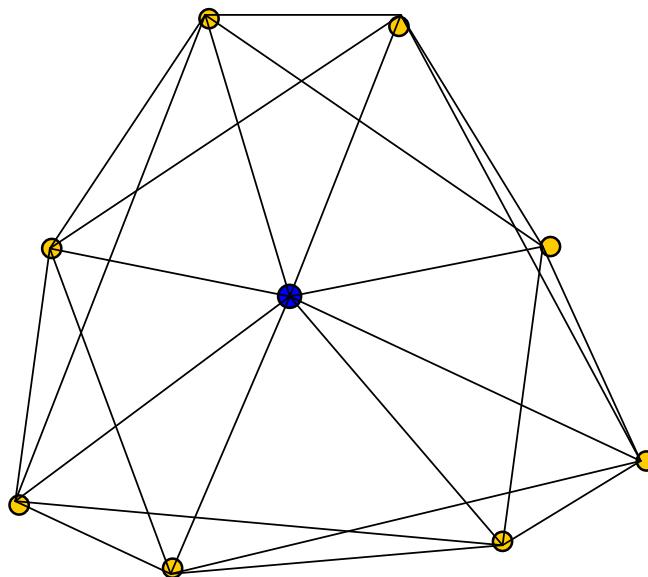
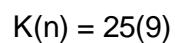
$$\begin{aligned} K &= 6[5]-1-18 = 11 \\ K(n) &= 11(6) \\ S &= 4n+2 \\ \text{CLOSO, } &[\text{M}6] \end{aligned}$$



$$K = 8+3 = 11$$



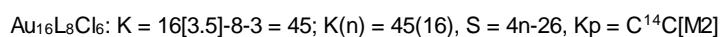
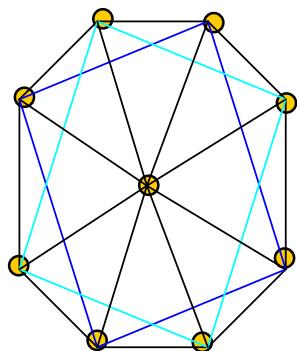
ISOMERISM



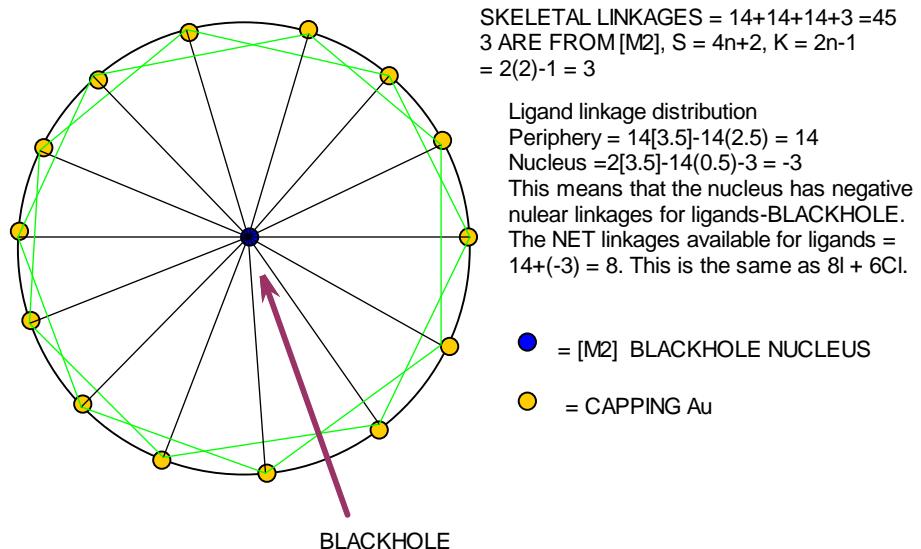


ISOMERISM

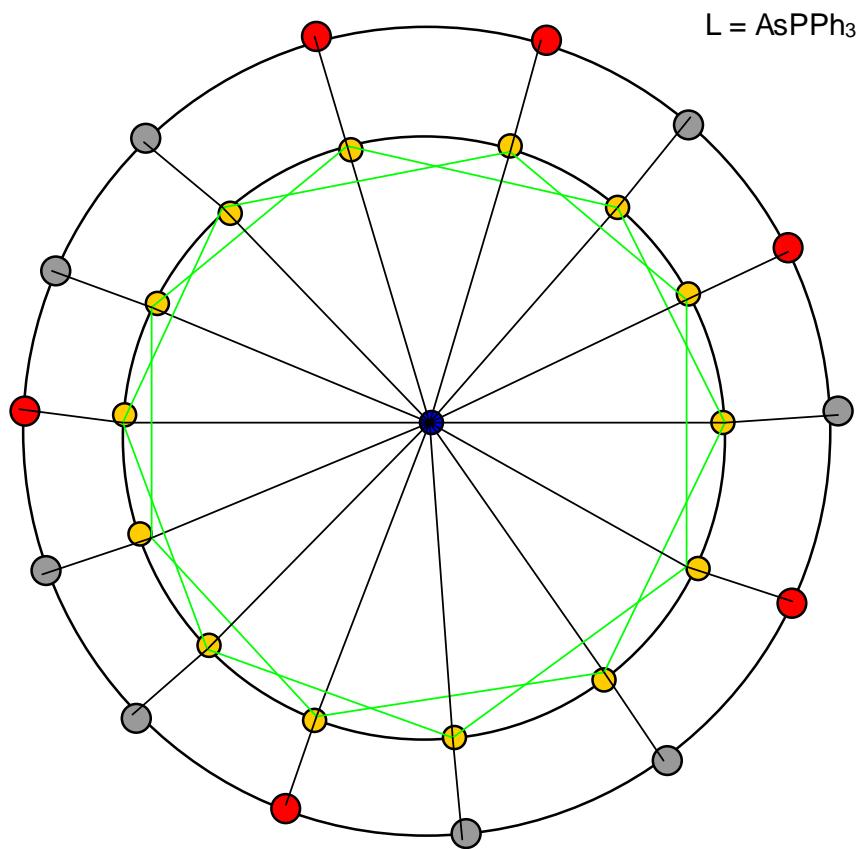
$$K_p = C^8C[M1] \quad K(n) = 25(9)$$



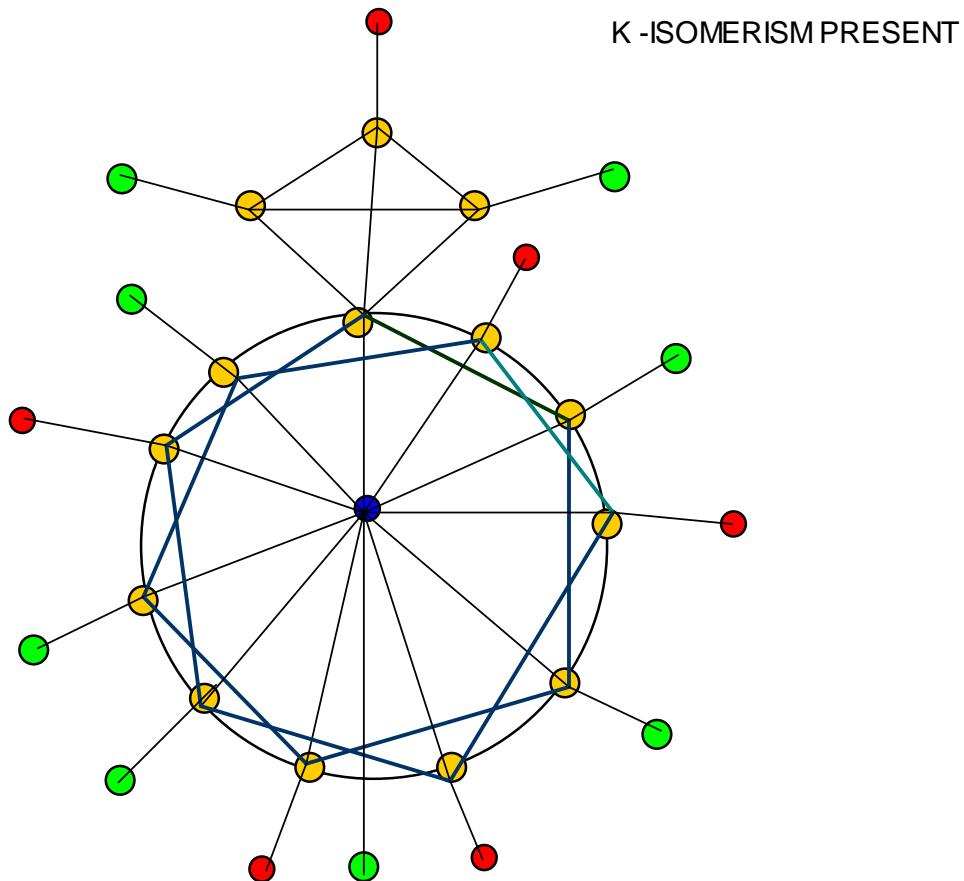
K ISOMERISM PRESENT AS WELL AS A BLACKHOLE NUCLEUS



$\text{Au}_{16}\text{L}_8\text{Cl}_6$: $K = 16[3.5]-8-3 = 45$; $K(n) = 45(16)$, $S = 4n-26$, $K_p = \text{C}^{14}\text{C}[\text{M}2]$



$\text{Au}_{16}\text{L}_8\text{Cl}_6$: $K = 16[3.5]-8-3 = 45$; $K(n) = 45(16)$, $S = 4n-26$, $K_p = \text{C}^{14}\text{C}[\text{M}2]$



POSSIBLE LIGAND DISTRIBUTIONS

DECAPPING CLUSTER SERIES:- $K_p = \text{C}^y\text{C}[\text{M}x]\text{capping}$

During the course of developing the $14n/4n$ series method for categorizing clusters, a capping symbol $K_p = \text{C}^y\text{C}[\text{M}x]$ was introduced. This is easily illustrated by the scheme SC-7.

SC-7

| $S = 4n+q$ | $4n+10$ | $4n+8$ | $4n+6$ | $4n+4$ | $4n+2$ | $4n+0$ | $4n-2$ | $4n-4$ |
|---------------------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|-------------------------|-------------------------|
| | KLADO | HYPHO | ARACHNO | NIDO | CLOSO | MONOCP | BICAP | TRICAP |
| $K_p = \text{C}^y\text{C}[\text{M}x]$ | C^4C | C^3C | C^2C | C^1C | C^0C | C^1C | C^2C | C^3C |
| | $4n-6$ | $4n-8$ | $4n-10$ | $4n-12$ | $4n-14$ | $4n-16$ | $4n-18$ | $4n-20$ |
| | TETRACP | PENTACP | HEXACP | C^7C | C^8C | C^9C | C^{10}C | C^{11}C |
| $K_p = \text{C}^y\text{C}[\text{M}x]$ | C^4C | C^5C | C^6C | | | | | |

Previously, the series were capturing clusters which were mono-capped, bi-capped, tri-capped, and so on (Kiremire, 2015, 2016b). The symbol was not extended to the lower series such as CLOSO, NIDO, ARACHNO, and KLAPO. According to the series, the capping or de-capping step involves one skeletal element ($\Delta n = 1$) and three skeletal linkages ($\Delta K = 3$). Looking at the symbol, $K_p = \text{C}^y\text{C}[\text{M}x], y=1$ when $S = 4n+0$, then $S = 4n-2, y=2, 4n-4, y=3$, etc. Moving backwards, from $S = 4n+0, y=1$, then for $S = 4n+2$, we can set the value of $y = 0$ and so the capping symbol will be $K_p = \text{C}^0\text{C}[\text{M}x]$. Further movement backwards to $S = 4n+4, y=-1$, hence, $K_p = \text{C}^{-1}\text{C}[\text{M}x]$. More backward movement, the capping symbol will be as indicated in the Table 4 and SC-7. The table numerically represents the concept (Rudolph, 1976) of correlating borane polyhedral geometrical structures.

Table 4. Decapping Series

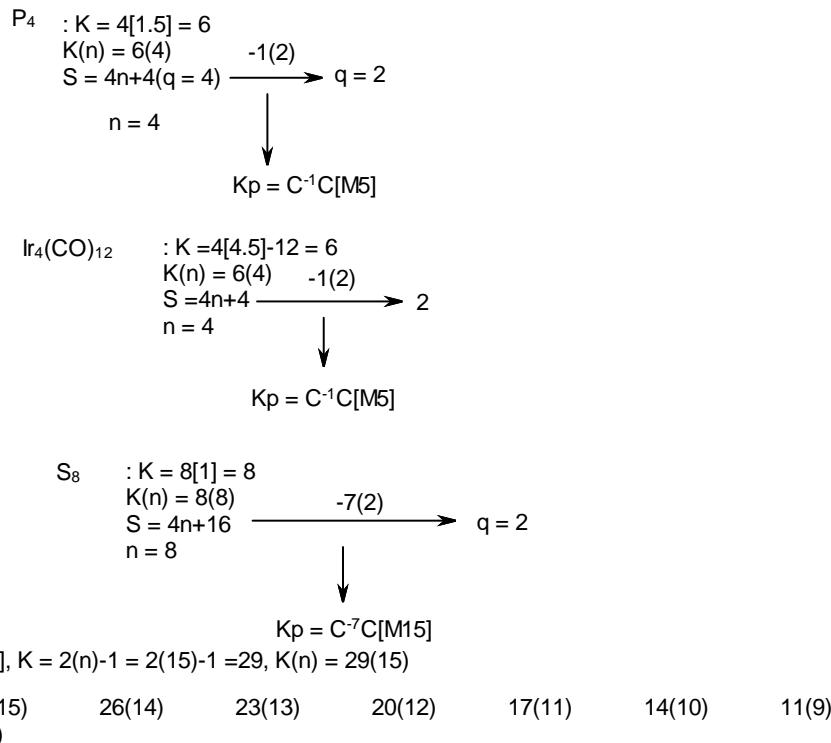
| [M12] | K(n) | [M11] | K(n) | [M10] | K(n) | [M9] | K(n) | |
|-----------------|-----------------------------|-------------|------------------------|-------------|------------------------|-------------|-----------------------|-------|
| C ⁰ | C ⁰ C[M12] | 23(12) | C ⁰ C[M11] | 21(11) | C ⁰ C[M10] | 19(10) | C ⁰ C[M9] | 17(9) |
| C ⁻¹ | C ⁻¹ C[M12] | 20(11) | C ⁻¹ C[M11] | 18(10) | C ⁻¹ C[M10] | 16(9) | C ⁻¹ C[M9] | 14(8) |
| C ⁻² | C ⁻² C[M12] | 17(10) | C ⁻² C[M11] | 15(9) | C ⁻² C[M10] | 13(8) | C ⁻² C[M9] | 11(7) |
| C ⁻³ | C ⁻³ C[M12] | 14(9) | C ⁻³ C[M11] | 12(8) | C ⁻³ C[M10] | 10(7) | C ⁻³ C[M9] | 8(6) |
| C ⁻⁴ | C ⁻⁴ C[M12] | 11(8) | C ⁻⁴ C[M11] | 9(7) | C ⁻⁴ C[M10] | 7(6) | C ⁻⁴ C[M9] | 5(5) |
| C ⁻⁵ | C ⁻⁵ C[M12] | 8(7) | C ⁻⁵ C[M11] | 6(6) | C ⁻⁵ C[M10] | 4(5) | C ⁻⁵ C[M9] | 2(4) |
| C ⁻⁶ | C⁻⁶C[M12] | 5(6) | C ⁻⁶ C[M11] | 3(5) | | | | |
| C ⁻⁷ | C ⁻⁷ C[M12] | 2(5) | C ⁻⁷ C[M11] | 0(4) | | | | |

| | [M8] | K(n) | [M7] | K(n) | [M7] | K(n) |
|-----------------|---------------------------|--------------|----------------------|--------------|----------------------|--------------|
| C ⁰ | C⁰[M8] | 15(8) | C ⁰ [M7] | 13(7) | C ⁰ [M7] | 13(7) |
| C ⁻¹ | C ⁻¹ [M8] | 12(7) | C ⁻¹ [M7] | 10(6) | C ⁻¹ [M7] | 10(6) |
| C ⁻² | C ⁻² [M8] | 9(6) | C ⁻² [M7] | 7(5) | C ⁻² [M7] | 7(5) |
| C ⁻³ | C ⁻³ [M8] | 6(5) | C ⁻³ [M7] | 4(4) | C ⁻³ [M7] | 4(4) |
| C ⁻⁴ | C⁻⁴[M8] | 3(4) | C ⁻⁴ [M7] | 1(3) | C ⁻⁴ [M7] | 1(3) |

| | [M6] | K(n) | [M5] | K(n) | [M4] | K(n) | [M3] | K(n) | [M2] | K(n) |
|-----------------|---------------------------|--------------|----------------------|-------------|----------------------|-------------|----------------------|-------------|----------------------|-------------|
| C ⁰ | C⁰[M6] | 11(6) | C ⁰ [M5] | 9(5) | C ⁰ [M4] | 7(4) | C ⁰ [M3] | 5(3) | C ⁰ [M2] | 3(2) |
| C ⁻¹ | C ⁻¹ [M6] | 8(5) | C ⁻¹ [M5] | 6(4) | C ⁻¹ [M4] | 4(3) | C ⁻¹ [M3] | 2(2) | C ⁻¹ [M2] | 0(1) |
| C ⁻² | C ⁻² [M6] | 5(4) | C ⁻² [M5] | 3(3) | C ⁻² [M4] | 1(2) | | | | |
| C ⁻³ | C⁻³[M6] | 2(3) | C ⁻³ [M5] | 0(2) | | | | | | |

Table 5. Some of Rudolph Type of Series and Corresponding Boran

| [M12] | K(n) | S | F _B | [M6] | K(n) | S | F _B |
|-----------------------------|-------------|--------------|---|----------------------|-------|------|--|
| C ⁰ C[M12] | 23(12) | 4n+2 | [BH](12)+2e = B ₁₂ H ₁₂ ²⁻ | C ⁰ [M6] | 11(6) | 4n+2 | [BH](6)+2e = B ₆ H ₆ ²⁻ |
| C ⁻¹ C[M12] | 20(11) | 4n+4 | [BH](11)+4H = B ₁₁ H ₁₅ | C ⁻¹ [M6] | 8(5) | 4n+4 | [BH](5)+4H = B ₅ H ₉ |
| C ⁻² C[M12] | 17(10) | 4n+6 | [BH](10)+6H = B ₁₀ H ₁₆ | C ⁻² [M6] | 5(4) | 4n+6 | [BH](4)+6H = B ₄ H ₁₀ |
| C ⁻³ C[M12] | 14(9) | 4n+8 | [BH](9)+8H = B ₉ H ₁₇ | C ⁻³ [M6] | 2(3) | 4n+8 | [BH](3)+8H = B ₃ H ₁₁ |
| C ⁻⁴ C[M12] | 11(8) | 4n+10 | [BH](8)+10H = B ₈ H ₁₈ | | | | |
| C ⁻⁵ C[M12] | 8(7) | 4n+12 | [BH](7)+12H = B ₇ H ₁₉ | | | | |
| C⁻⁶C[M12] | 5(6) | 4n+14 | [BH](6)+14H = B₆H₂₀ | | | | |



SC-8

Appendix-1

| Skeletal k Values of Main Group Elements | | | | | | | |
|--|------------------|------------|----|----|----|----|----|
| Group | Series, S = 4n+q | k = 2n-q/2 | Li | Na | K | Rb | Cs |
| 1 | 4n-3 | 3.5 | | | | | |
| 2 | 4n-2 | 3 | Be | Mg | Ca | Sr | Ba |
| 3 | 4n-1 | 2.5 | B | Al | Ga | In | Tl |
| 4 | 4n+0 | 2 | C | Si | Ge | Sn | Pb |
| 5 | 4n+1 | 1.5 | N | P | As | Sb | Bi |
| 6 | 4n+2 | 1 | O | S | Se | Te | Po |
| 7 | 4n+3 | 0.5 | F | Cl | Br | I | At |
| 8 | 4n+4 | 0 | Ne | Ar | Kr | Xe | Rn |

Appendix-2

| Skeletal k Values of Transition Metals | | | | |
|--|------|-------|-------------|------------|
| 3d-TM | 4d - | 5d-TM | Series, S = | k = 2n-q/2 |
| * | TM* | * | 4n+q | |
| Sc | Y | La | 4n-11 | 7.5 |
| Ti | Zr | Hf | 4n-10 | 7 |
| V | Nb | Ta | 4n-9 | 6.5 |
| Cr | Mo | W | 4n-8 | 6 |
| Mn | Tc | Re | 4n-7 | 5.5 |
| Fe | Ru | Os | 4n-6 | 5 |
| Co | Rh | Ir | 4n-5 | 4.5 |
| Ni | Pd | Pt | 4n-4 | 4 |
| Cu | Ag | Au | 4n-3 | 3.5 |
| Zn | Cd | Hg | 4n-2 | 3 |

4. Conclusion

A collection of known golden clusters have been analyzed and categorized using skeletal numbers. A large percentage of them are centered around [M0], [M1] and [M2] closo-based axes. The [Mx] may be regarded as similar to groups of elements in the periodic table. The clusters which lie on the closo lines [Mx], $x \leq 0$, have a tendency of possessing metallic character. In this connection, the golden clusters are closer to the metallic region of metallic clusters than that of non-metallic. A concept of a black-hole nucleus has been introduced as well as that of numerical categorization of clusters which lie lower than the closo base line. The two dimensional ideal shapes of clusters have been sketched using graph theory derived from the 4n series method.

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