Carbonyl Chalcogenides Clusters Existing as Disguised Forms of Hydrocarbon Isomers

Enos Masheija Rwantale Kiremire

Correspondence: Enos Masheija Rwantale Kiremire, Department of Chemistry and Biochemistry, University of Namibia, Private Bag 13301, Windhoek, Namibia. E-mail: kiremire15@yahoo.com

Abstract

The 4n Series Method has been utilized to categorize, analyze and predict structures for transition metal carbonyl, borane, hydrocarbon and Zintl ion clusters. The method is being extended to study carbonyl chalcogenide clusters. Adequate examples have been given to demonstrate the application of the 4n series method to categorize clusters and where possible predict their possible skeletal structures. In this paper, the method is being applied to the study of carbonyl chalcogenide cluster complexes. What has been found is the striking structural similarity of a wide range of carbonyl chalcogenide clusters to those of corresponding hydrocarbon clusters. It was observed that when a derived hydrocarbon from a cluster, $F_{CH} = C_nH_q$, is such that n<q, the cluster portrays structural similarity with an equivalent hydrocarbon. On the other hand when n>q, the 'hydrocarbon character' becomes reduced and the typical cluster tendencies increase. When n = q, the situation becomes more or less a borderline case. When q=0, then $F_{CH} = C_n$. When the series becomes bi-capped or more, then the equivalent carbon cations are obtained.

Keywords: clusters, hydrocarbons, fragments, 4n- series, isolobal, capping -clusters, hydrocarbon- character, cations

1. Introduction

Although boron and carbon atoms are next to each other in the periodic table, the boranes and their relatives are dominated by polyhedral shapes unlike the hydrocarbon analogues (Cotton, and Wilkinson, 1980). Arising from the unique polyhedral structures and potential applications, the clusters have continued to fascinate many scientists (Lipscomb, 1963; Wade, 1971, 1976; Pauling, 1977; Mingos, 1972, 1984; Hawthorne, et al, 1999; Jemmis, 2005; Jemmis, et al, 2006; Jemmis, et al, 2008; Welch, 2013). Wade-Mingos rules have been exceedingly useful in categorizing and predicting the shapes of clusters (Wade, 1971, 1976; Mingos, 1972, 1984; Welch, 2013). During the study of the metal carbonyl clusters to determine the nature of their constitution, it was discovered that they generally obey the 14n rule while the main group clusters obey the 4n rule and that the two systems are interrelated via the isolobal relationship (Hoffmann, 1982; Kiremire, 2014, 2015, 2016). Furthermore, it was discerned that clusters could readily be categorized and their shapes predicted using the 4n series method (Kiremire, 2015, 2016).

2. Results and Discussion

2.1 The role of 4n Series Method and Its Unification of Clusters

In order to understand the application of series approach to categorize clusters and how they are interlinked, it is important to give some examples as illustrations. The application of series may be regarded as 'wearing a new type of spectacles' that makes it possible to see more details in a chemical fragment. The series method utilizes a simple algebra of valence electrons of fragments and ligands. The series formula which is in the form of S = 4n+q contains useful information. It provides the number valence electrons contained within a cluster. It can be used to categorize a cluster or generate another type of cluster as required. On closer analysis of series as they are applied to transition metal carbonyls, boranes, heteroboranes, metalloboranes, hydrocarbons and Zintl ions (Greenwood & Earnshaw, 1998), it is readily discerned that clusters are all interrelated. This is summarized in Scheme 1.
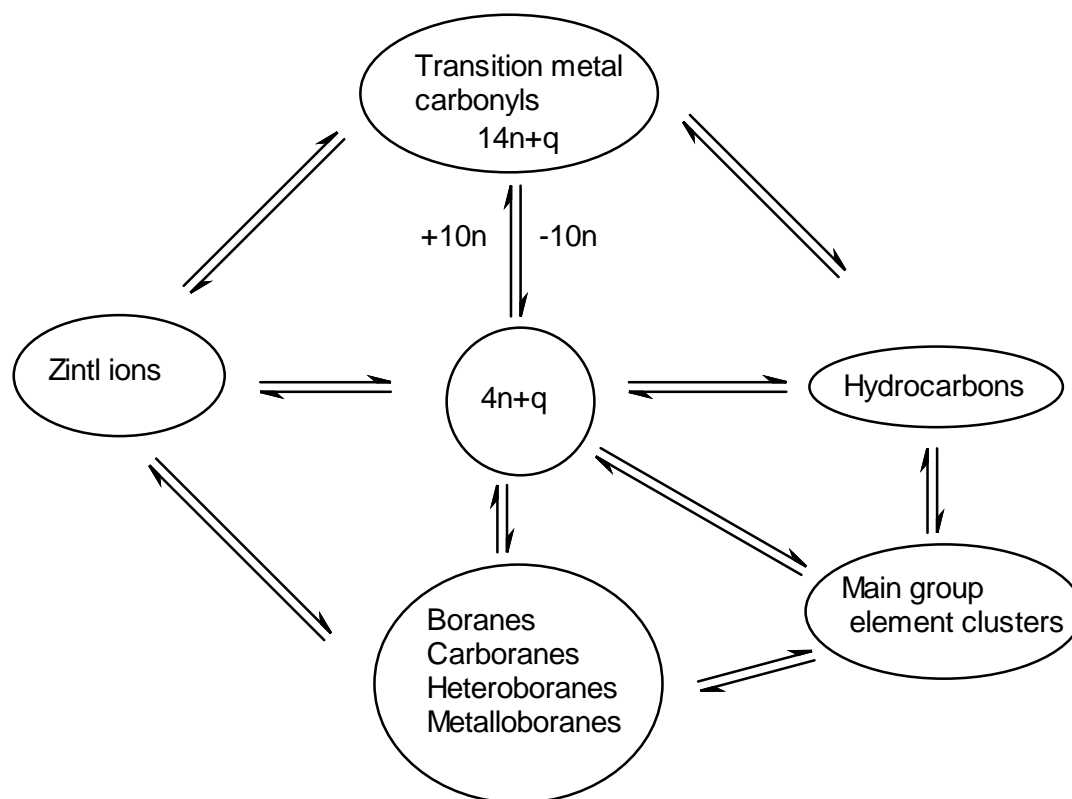
Scheme 1. Interrelationship among clusters

Selected examples of different types of clusters have been taken and transformed into equivalent hydrocarbon clusters for illustrations. These are given in 2.2 to 2.7. They demonstrate how a cluster formula may be decomposed into a series formula from which other clusters may be generated. The details of the method have been covered elsewhere (Kiremire, 2015, 2016). Furthermore, sufficient explanation is provided in each of the examples given.
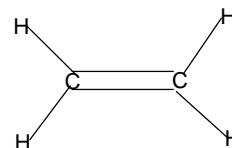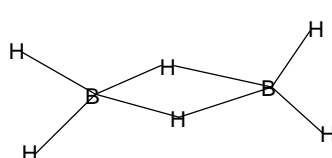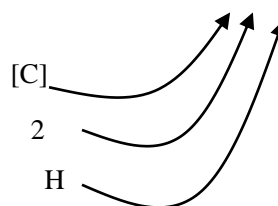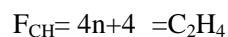
2.2 B_2H_6

$2[BH] \rightarrow 2[3+1] = 2[4+0] \rightarrow 4n+0(n=2)$; $F_{CH} = 4n+4$

$\qquad 4(H) \rightarrow 0+4(n=0)$

$\qquad\quad S = 4n+4(n=2)$

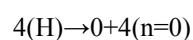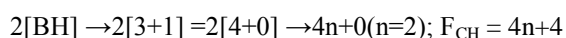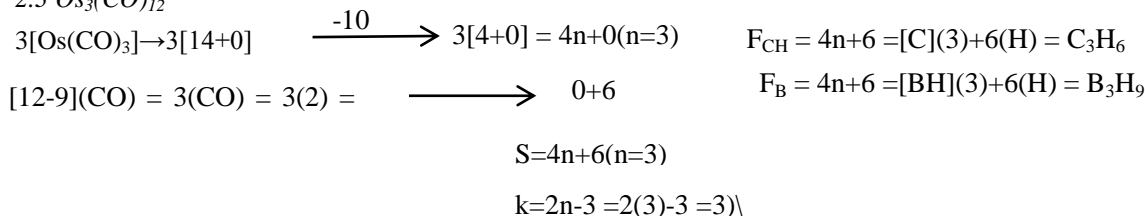$F_{CH} = 4n+4 = C_2H_4$

[C]

2

H
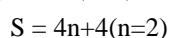
Figure F-1. Shape of B_2H_6 Figure F-2. Shape of C_2H_4

The B_2H_6 molecule belongs to the nido clan series. Its shape is shown in F-1. Its hydrocarbon isomer, C_2H_4 is shown in F-2. The cluster k value is given by $k = 2n-2 = 2(2)-2 = 2$. That means the two skeletal atoms are linked by 2 bonds. In case the of borane (F-1), the bridging H atoms supply the additional electrons to complete the double bonds.
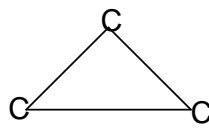
2.3 $Os_3(CO)_{12}$

$3[Os(CO)_3] \rightarrow 3[14+0]$ $\xrightarrow{-10}$ $3[4+0] = 4n+0(n=3)$ $F_{CH} = 4n+6 = [C](3)+6(H) = C_3H_6$

$[12-9](CO) = 3(CO) = 3(2) =$ $\xrightarrow{\quad}$ $0+6$ $F_B = 4n+6 = [BH](3)+6(H) = B_3H_9$

$S = 4n+6(n=3)$

$k = 2n-3 = 2(3)-3 = 3\backslash$

The skeletal shape of the $Os_3(CO)_{12}$ is a triangle. This is shown in Figure F-3. The corresponding 'mapped' isomeric hydrocarbon isomer is given in Figure F-4. When the hydrogen atoms are included in the hydrocarbon skeletal structure, we get figure F-5.
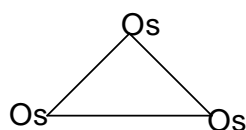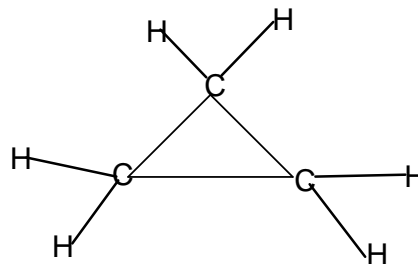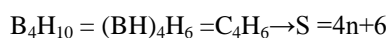

k = 3

F-3

k = 3

F-4

F-5

The reason for mapping the hydrocarbon isomer or designing the sketch to be similar to that of the parent cluster is that the hydrocarbon may have several other possible isomers.

2.4 B_4H_{10}

$B_4H_{10} = (BH)_4H_6 = C_4H_6 \rightarrow S = 4n+6$

The borane cluster can directly be transformed into a hydrocarbon cluster by factoring the formula into [BH] fragments as illustrated in the case of B_4H_{10} without going through the series formula route. This is because [BH] $\leftrightsquigarrow$ [C] in terms valence electron content. The derivation of the series formula from a hydrocarbon cluster is also easy as a cluster C_n is simply $S = 4n+0$. The hydrogen atoms in the hydrocarbon simply give us the variable figure after 4n. The cluster k value $= 2n-2 = 2(4)-3 = 5$. A skeletal sketch of B_4H_{10} is given in F-6 and that of the C_4H_6 isomer in F-7 including the H atoms.

k = 5

k = 5

F-7

F-6
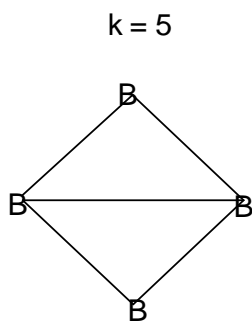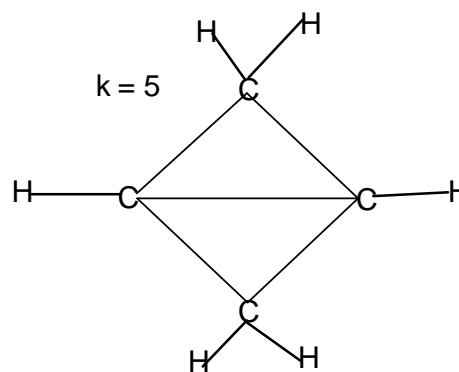
2.5 $Re_5(C)(H)(CO)_{16}^{2-}$

$$5[Re(H)(CO)_3] \rightarrow 5[14+0] \xrightarrow{-10} 5[4+0] \rightarrow S = 4n+0(n=5)$$

$$[16-15](CO) = 1(CO) \longrightarrow 0+2(n=0)$$

$$[1-5](H) = -4(H) \longrightarrow 0-4(n=0)$$

$$C \longrightarrow 0+4(n=0)$$

$$q \longrightarrow 0+2(n=0) \quad q = charge$$

$$S = 4n+4(n =5)$$

$$k = 2n-2 = 2(5)-2 = 8(n =5)$$

Since S =4n+4, the cluster belongs to the nido clan of clusters.The corresponding hydrocarbon and borane clusters can readily be derived from the series formula above. Thus, $F_{CH} = 4n+4 = [C](5)+4(H) = C_5H_4$ and $F_B = [BH](5)+4H = B_5H_9$. The sketches of the skeletal shapes of the rhenium cluster, $Re_5(C)(H)(CO)_{16}^{2-}$, the corresponding borane cluster, B_5H_9 and the hydrocarbon, C_5H_4 clusters are given in F-8, F-9 and F-10 respectively. The hydrocarbon isomer has to be mapped according to the rhenium cluster as was done in F-7 above.
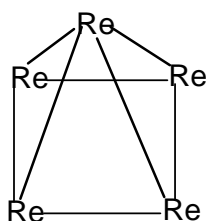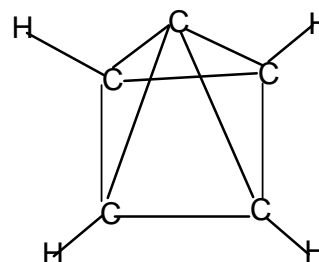

F-8
k =8
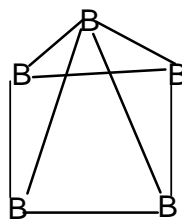
F-9
k =8

F-10
k =8

As can be seen from F-10, the C_5H_4 isomer is very much strained especially the pyramical-apex carbon atom which has no hydrogen attachment. Some interesting work on strained hydrocarbons has been going on for sometime (Stohrer and Hoffmann, 1972; Carnes, et al, 2008).

2.6 $Rh_5(CO)_{15}^-$ versus $Os_5(CO)_{15}^{2-}$

Using the same procure as in 2.2 to 2.5, $Rh_5(CO)_{15}^-$ belongs to S =4n+6 (arachno)while $Os_5(CO)_{15}^{2-}$ belongs to S =4n+2(closo) series. The 4n+6(n=5) can be transformed into B_5H_{11} (C_5H_6, k =7)while S = 4n+2 converts into $B_5H_5^{2-}$ (C_5H_2, k =9). $Rh_5(CO)_{15}^-$ has been described as having a trigonal bipyramid shape with elongated axial lengths while the $Os_5(CO)_{15}^{2-}$ cluster was described as having a regular trigonal bipyramid shape (Teo, et al, 1984). This is not surprising as they belong to two different series with different k values. Proposed skeletal shapes modeled by their hydrocarbons are given in F-11 and F-12.

F-11

F-12

Elongated trigonal bipyramid   Regular trigonal bipyramid
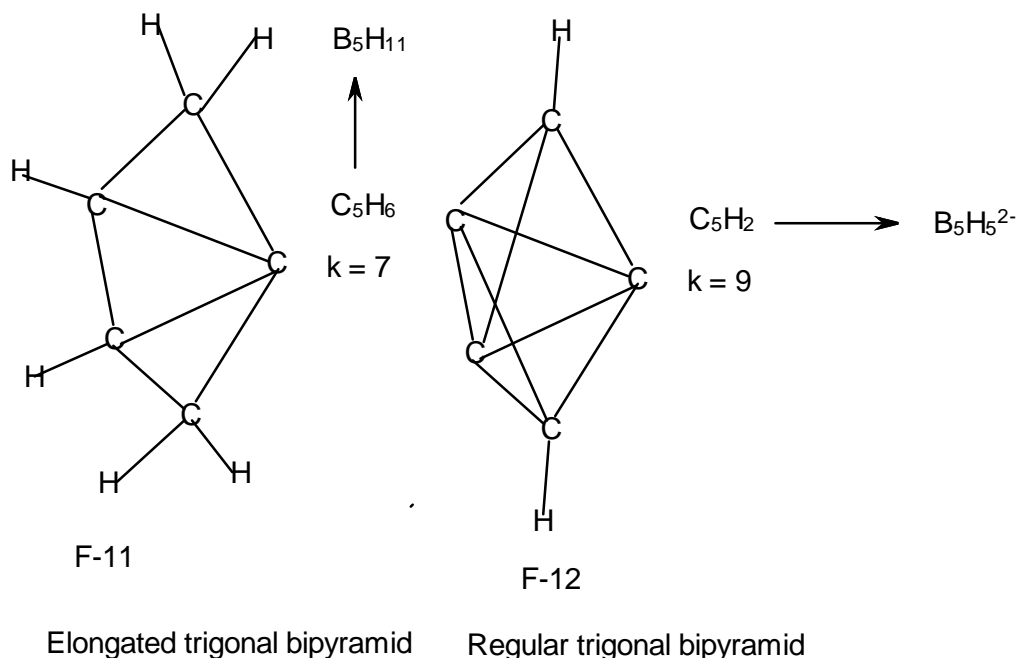
The hydrocarbon isomers F-11 and F-12 are very much strained.

2.7 Octahedral Clusters: $Re_6(C)(CO)_{19}^{2-}$, $Os_6(CO)_{18}^{2-}$, $Rh_6(CO)_{16}$, $B_6H_6^{2-}$

The range of octahedral clusters is large. The above examples have been selected to be used as demonstrations of the power of series.

2.7.1 $Re_6(C)(CO)_{19}^{2-}$

$6[Re(H)(CO)_3]$

$\rightarrow 6[14+0] = 6[14+0-10] = 6[4+0] \rightarrow 4n+0(n=6)$.

$$[0-6](H) \rightarrow 0-6(n=0)$$

$$[19-18](CO) = 1(CO) \rightarrow 0+2(n=0)$$

$$(C) \rightarrow 0+4(n=0)$$

$$q \rightarrow 0+2(n=0), q = charge$$

$$S = 4n+2(n=6), \text{ member of a closo clan of series.}$$

In deriving a series formula, it is found easier to use fragments whose electron contents which are 14(transition metals) or 4(for main group elements). In creating suitable fragments, balancing ligands such as H or CO which are not in the original formula of the cluster may be added and then subtracted later as in this example. The ligands which are not defined as part of the skeletal elements are assigned the value of 0. The transition metal clusters $Os_6(CO)_{18}^{2-}$ and $Rh_6(CO)_{16}$ are dealt with in the same way as $Re_6(C)(CO)_{19}^{2-}$ cluster and all of them belong to the $4n+2$ series.
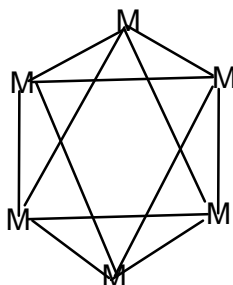
2.7.2 $B_6H_6^{2-}$

$6[BH] \rightarrow 6[3+1] = 6[4+0] \rightarrow 4n+0(n=6)$

$$q \rightarrow 0+2(n=0)$$

$$S = 4n+2(n=6)$$

This means that the clusters $Re_6(C)(CO)_{19}^{2-}$, $Os_6(CO)_{18}^{2-}$, $Rh_6(CO)_{16}$ and $B_6H_6^{2-}$ belong to the same family of the clan of series $S = 4n+2$ (n = 6, closo). They all portray a skeletal shape of an octahedral geometry (G-1).

G-1. Octahedral geometry, O_h

Using the above series formula we can derive a hydrocarbon analogue of the clusters. This is given by the formula F_{CH} = 4n+2 = [C](6)+2(H) = C_6H_2. It will be interesting to map C_6H_2 cluster into a skeletal sketch of an octahedral geometry. One of the possible isomers is shown in F-13.

k = 11
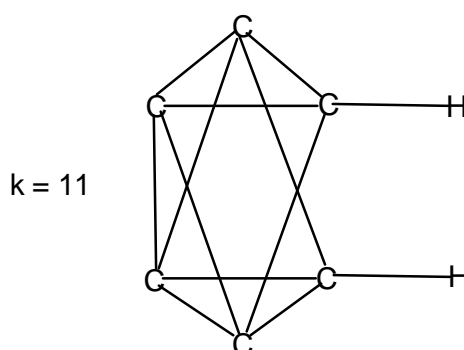
F-13

According to the cluster series S = 4n+2 and k =2n-1. If n = 6, then k = 2(6)-1 = 11. This means that C_6H_2 has 11 skeletal linkages.   When the two hydrogen atoms are included, we get the sketch of the isomer shown in F-13. The hydrocarbon isomer is clearly very strained. Another possible hypothetical skeletal isomer of C_6H_2 is given in F-14 and its hydrogen counterpart in F-15.

k = 11   k = 11
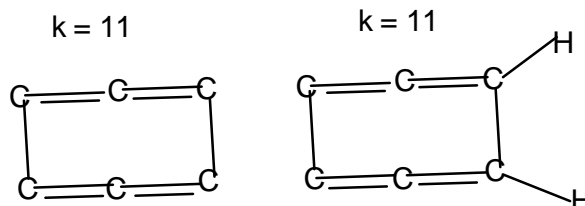
F-14   F-15

The skeletal linkages exclude those bonds which link the carbon atoms to the H atoms. What is also interesting for the hydrocarbon models such as F-11, F-12, F-13 and F-15 is that each of the carbon atoms obeys the 8-electron rule despite the severe strain of the configuration. The general series equation of the clusters may be represented as S = 4n+q. It appears that as q becomes smaller and smaller, the cluster becomes more and more strained as demonstrated by the corresponding hydrocarbon analogues. With this background, we can examine the carbonyl chalcogenide complexes using the 4n series method.

2.8 Categorization and Structural Prediction of Carbonyl Chalcogenides Using the 4n Series Method

The series method is being utilized to examine chemical systems including among others, atoms, molecules, fragments and clusters. In this paper, the method is being applied to analyze carbonyl chalcogenide complexes. The examples have been selected from various literature sources (Shieh, et al, 2003; Shieh, et al, 2012; Harlan, et al, 1996; Das, et al, 1997). The results of the samples analyzed are given in Table 1. Their series fall in the range of S= 4n-2 (bi-capped) to

S=4n+20. This can be compared with most common boranes which fall in the range S = 4n+2 (closo) to S =4n+8 (hypho). When the digit after 4n is large, this implies that some of the chalcogenide carbonyl clusters behave like hydrocarbons. For instance $C_{10}H_{22}$, belongs to the series S = 4n+22. What is amazing is that the structures of chalcogenide carbonyl clusters with q values such as 6, 8, 10, and 12 resemble some of the isomers of the analogous hydrocarbons. Selected examples are given in CCG-1 to CCG-5 below. The cluster $TeCr_2(Cp)_2(CO)_4$, S = 4n+4(n=3) and its equivalent hydrocarbon is C_3H_4. The cluster belongs to the nido clan series with k value of 4. The $TeCr_2$ skeletal fragment is found to have two double bonds of Cr atoms linked to Te element Cr=Te=Cr. This is similar to the allene isomer of C_3H_4. This is illustrated in CCG-1. The CCG-2 cluster, $Se_2Cr(Cp)(CO)_2{}^-$, belongs to the arachno series S = 4n+6 with k = 3. In this case, the Se_2Cr skeletal elements form a triangle. The series correspond to C_3H_6 hydrocarbon. The triangular shape of Se_2Cr fragment corresponds to cyclopropane which is one of the isomers of C_3H_6.These shapes are shown in CCG-2. The examples in CCG-3 to CCG-5 have been treated in the same manner. The striking similarity between some carbonyl clusters with hydrocarbons can further be demonstrated with the rhenium carbonyl cluster $Re_6H_5(CO)_{24}{}^-$(Housecroft, 2005). This cluster belongs to S =4n+12 series with k value of 6. The corresponding hydrocarbon is C_6H_{12}. The carbonyl cluster has been found to have a cyclohexane shape which is similar to one of the isomers of C_6H_{12} hydrocarbon. Due to the striking structural similarity of derived hydrocarbons with those of the corresponding carbonyl chalcogenides Table 1 comprising of 19 clusters was constructed.

2.9 Extractions from Table 1

2.9.1 *Origin of Conventional Hydrocarbon Series*

There is some useful information that can be derived from Table 1. If we keep the number of skeletal atoms (carbon elements) constant and vary the number of hydrogen atoms (ligands), we can get ranges of hydrocarbon series. For example, C_6H_{14}, C_6H_{12}, C_6H_{10}, C_6H_8, up to C_6. Such series of hydrocarbon clusters are shown in Table 2. From Table 1, one of the carbonyl complex has been found to belong to the series S = 4n-2. Since n=8, this gives us the hydrocarbon analogue of the form C_8-2H. This type of hydrocarbon can be represented by $C_8{}^{2+}$ cation. The series 4n-2 represents a clan of bi-capped series, Cp = C^2C[M-6]. The capping symbol means that there are 2 skeletal atoms capping onto 6 atoms which belong to 4n+2 closo series with an octahedral geometry. The first three columns on the left of Table 2 represent the well-known alkane, alkene and alkyne series respectively.

2.9.2 Hydrocarbons Arranged according to 4n Series

When Table 2 so constructed is scrutinized, we can see another type of series along the diagonal. These include among others, the series C, C_2, C_3, C_4, C_5, C_6 and so on and others CH_2, C_2H_2, C_3H_2, C_4H_2, C_5H_2, C_6H_2 and so on. These two examples correspond to mono-capped and closo series respectively. A sample of these series are given in Table 3.

2.9.3 Skeletal Linkages (k values) Arranged according to 4n Series

When Table 3 is also analyzed, it is observed that the k values also form series which represent the hydrocarbons in the table. This is given in Table 4. If we take M-2 in Table 4 and move from left to right we get k =4(4n+0), 3(4n+2), 2(4n+4) and 1 for (4n+6). These values correspond to C≡C, C≡C, C=C and C—C bonds respectively. The hydrocarbons having the triple, double and single carbon-carbon bonds are well known. However, the quadruple bond is still controversial (Shaik, et al, 2012) despite the fact that it was also predicted much earlier for C_2 and BeO(Teo, et al, 1984). Certain shapes may be recognized by looking at the series and their corresponding k values. For example, for M-3, k=3(4n+6) may represent cyclopropanes, M-4, k=6(4n+4) can correspond to tetrahedranes, k =4(4n+8),cyclobutanes, M-5; k =9(4n+2), trigonal bipyramid clusters, k=8(4n+4), square pyramid clusters, k =5(4n+10), cyclopentanes and for M-6; k =11(4n+2),octahedral clusters, k =10(4n+10), pentagonal pyramid, k =9(4n+6), benzenes and prismanes, and k =6(4n+12), cyclohexanes.
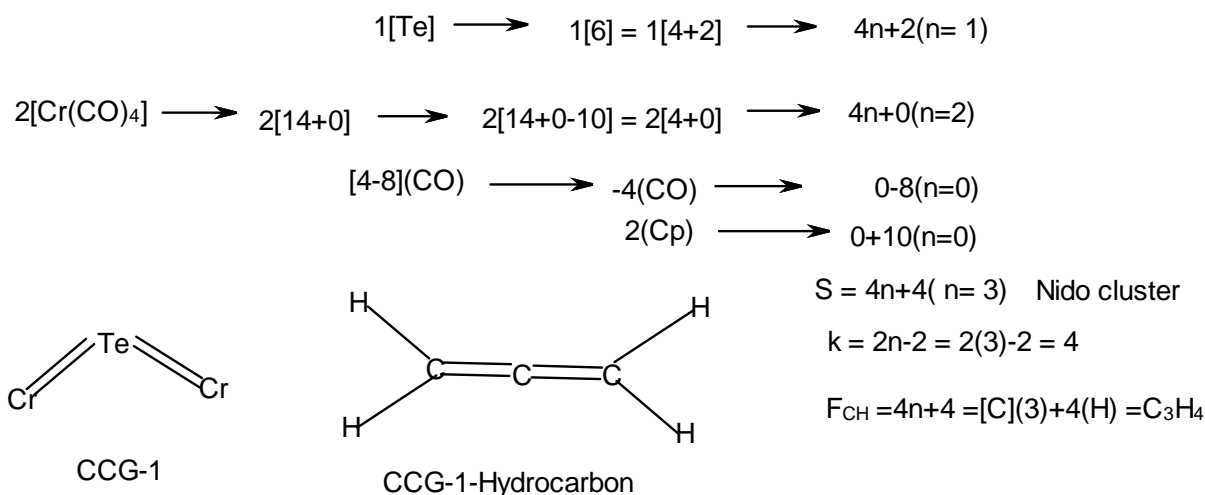
2.9.4 Rudolph System of Series (Upward Diagonal Relationship)

The Rudolph series of clusters are detected by looking at the diagonal of Table 4 upwards. Let us consider the following series: M-5; k =9 (4n+2), M-4; k =6(4n+4), M-3; and k =3(4n+6). The k values in this case, represent trigonal bipyramid, tetrahedral and trigonal planar clusters respectively. Another set to consider is M-6; k =11(4n+2), M-5; k = 8(4n+4), M-4; k=5(4n+6) and M-3; k=2(4n+8) represent octahedral, square planar and open M-3 cluster systems respectively. These series coincide with those of Rudolph system widely used to predict shapes of clusters together with Wade-Mingos rules (Rudolph, 1976; Wade, 1971).
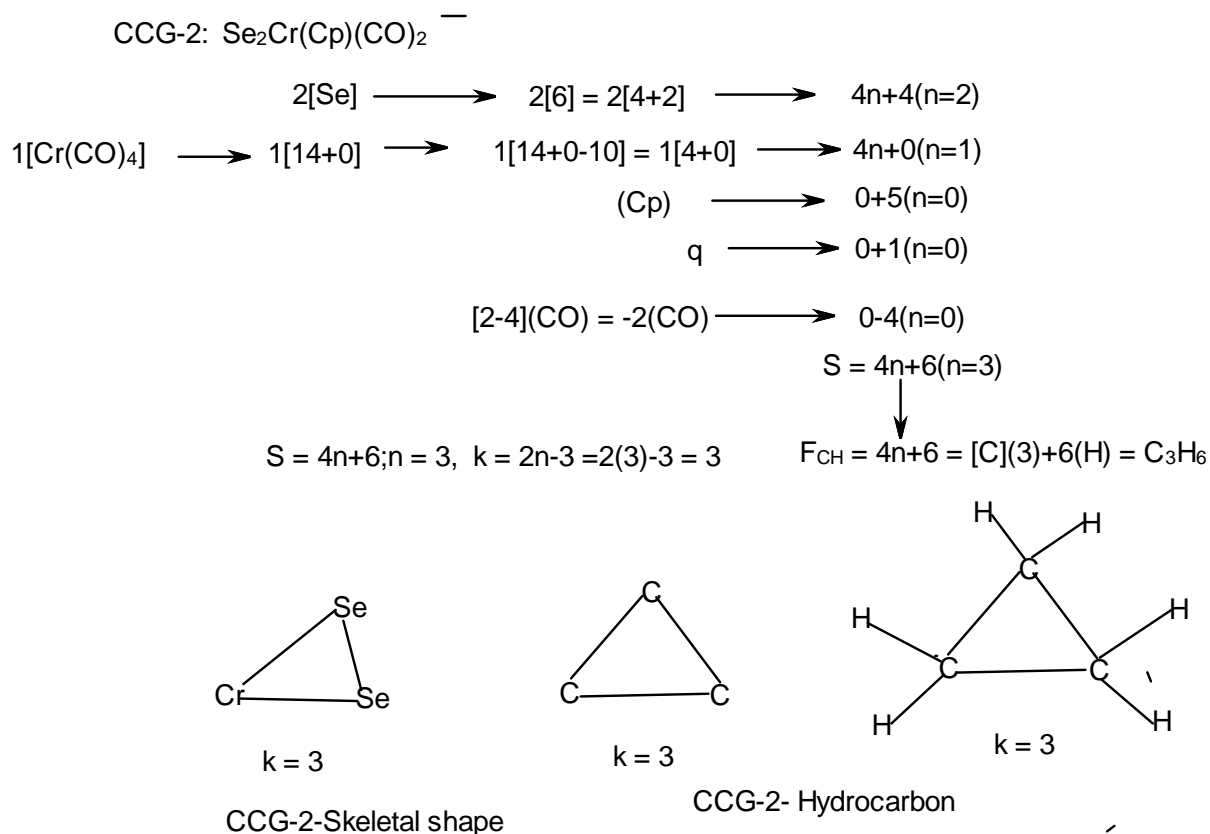
2.9.5 General Considerations of Hydrocarbon Clusters $F_{CH} = C_nH_q$

Transition metal carbonyl, boranes, Zintl ion and main group element clusters can readily be transformed into hydrocarbon analogue clusters. The hydrocarbon clusters so produced can be mapped onto the corresponding shapes of the clusters from which they were produced. This means that the parent cluster adopts a skeletal shape of one of the corresponding hydrocarbon isomers. Since hydrocarbon clusters are versatile and less bulky, they may be useful in
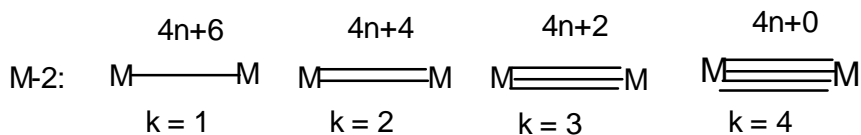
analyzing structural characteristics of clusters. A hydrocarbon cluster may be represented by the formula $F_{CH} = C_nH_q$. Hence, the corresponding series formula is $S = 4n+q$. As q becomes smaller and smaller, the k value increases more and more. This is clearly shown by the k values in Table 4. If we take some of the M-2 k values, for instance, $C_2(k =4) > C_2H_2(k =3) > C_2H_4(k=2) > C_2H_6(k=1) > C_2H_8(k=0)$. Thus, the k values decrease as the H ligands are added to the bi-skeletal cluster. This makes sense since the addition of 2H atoms to the C_2 fragment to form C_2H_2 molecule, two electrons from the C_2 are removed to participate in formation of the 2 C-H bonds resulting in the decrease of the k value from 4 to 3. The process continues until $C_2H_8(k =0)$ cluster is formed. The k = 0 value means that the fragment C_2H_8 is unstable and decomposes to generate the more stable molecules $2CH_4$ which obey the octet rule. The variation of k values horizontally is well illustrated in Table 4. By looking at the hydrocarbon clusters, it appears that if n is kept constant and q is increased, the 'hydrocarbon character' of the cluster increases. That means the k value of the cluster decreases as well. Clearly, the k value is sensitive to the electron density of the valence electrons around the skeletal atoms. As the electron density of the skeletal atoms increases, the k values decrease and vice-versa. As q increases relative to n, a stage is reached where k value of the cluster represents same linkages as the hydrocarbon fragment and both the carbonyl cluster and hydrocarbon molecule portray similar shapes. For instance a cluster with a formula $F_{CH} = C_5H_2$ and k =9 and a cluster with a formula $F_{CH} = C_5H_{10}$ and k= 5, the later system may portray a shape similar to a cyclopentane isomer. Hypothetically, the C_5H_2 is electronically equivalent to the unknown C_5^{2-} ion. However, the heavier tetrel elements $M_5^{2-}(M = Sn, Pb)$ in the form of Zintl ion clusters (Scharfe, et, al, 2010) are well known. Some of the possible skeletal shapes of M-2, M-3, M-4 and M-5 clusters are shown in Schemes 2 and 3. When clusters are analyzed more closely, and the ratio of number of valence skeletal electrons (V, based on 4n series) to the number of skeletal elements(n) is calculated for the clusters in Tables 1-3, it is found that , r =V/n ⩾ 5. Therefore, it appears that the "hydrocarbon character" starts when the ratio r =V/n ⩾ 5. This observation will be investigated further in the continued work. In a general hydrocarbon formula $F_{CH} = C_nH_q$, 'cluster character' tends to increase when n≫q. The 4n series can be viewed as a unifier that links up clusters such as boranes, carbonyls, hydrocarbons and Zintl ions (Scharfe, et al, 2010).
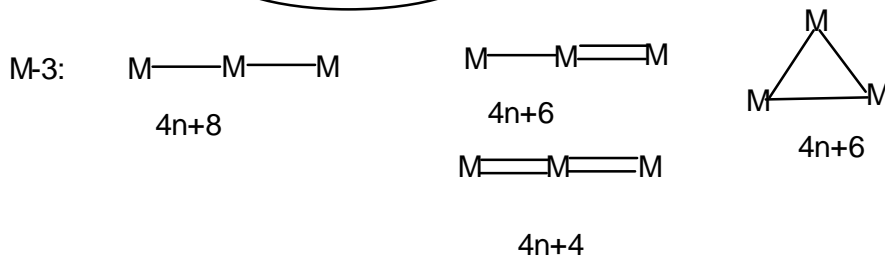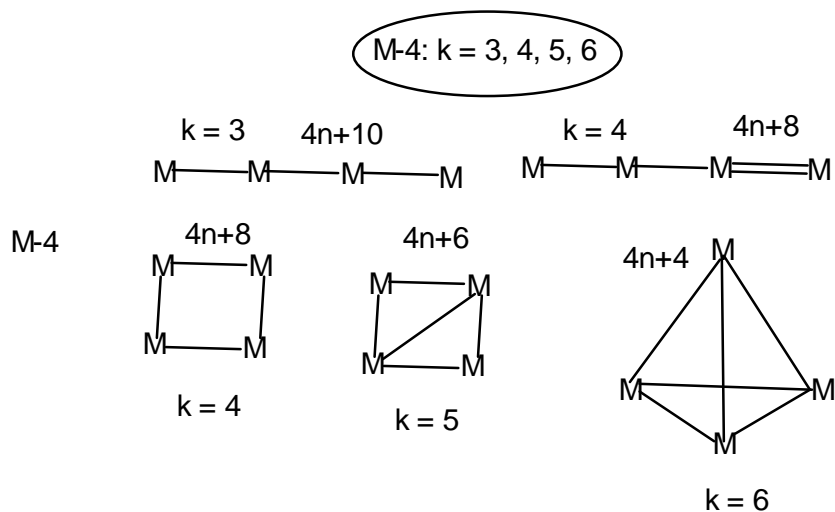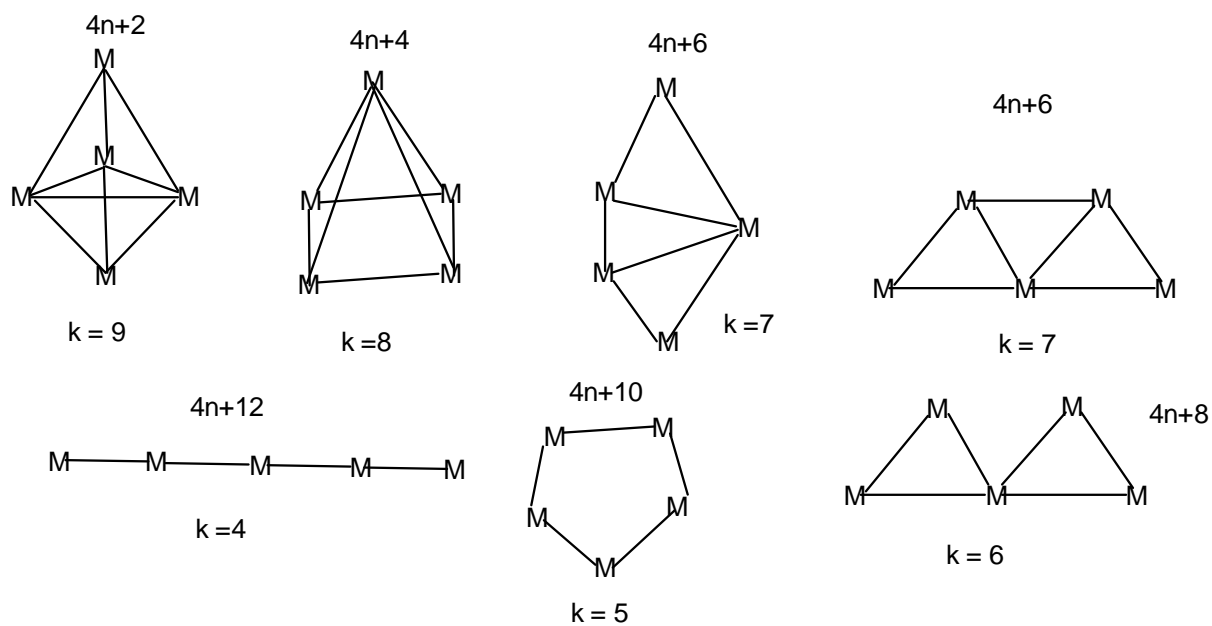
CCG-1: $TeCr_2(Cp)_2(CO)_4$

$1[Te] \longrightarrow 1[6] = 1[4+2] \longrightarrow 4n+2(n= 1)$

$2[Cr(CO)_4] \longrightarrow 2[14+0] \longrightarrow 2[14+0-10] = 2[4+0] \longrightarrow 4n+0(n=2)$

$[4-8](CO) \longrightarrow -4(CO) \longrightarrow 0-8(n=0)$

$2(Cp) \longrightarrow 0+10(n=0)$

$S = 4n+4(n= 3)$ Nido cluster

$k = 2n-2 = 2(3)-2 = 4$

$F_{CH} =4n+4 =[C](3)+4(H) =C_3H_4$

CCG-1

CCG-1-Hydrocarbon

CCG-2: $\overline{Se_2Cr(Cp)(CO)_2}$

$2[Se] \longrightarrow 2[6] = 2[4+2] \longrightarrow 4n+4(n=2)$

$1[Cr(CO)_4] \longrightarrow 1[14+0] \longrightarrow 1[14+0-10] = 1[4+0] \longrightarrow 4n+0(n=1)$

$(Cp) \longrightarrow 0+5(n=0)$

$q \longrightarrow 0+1(n=0)$

$[2-4](CO) = -2(CO) \longrightarrow 0-4(n=0)$

$S = 4n+6(n=3)$

$S = 4n+6; n = 3,\ k = 2n-3 = 2(3)-3 = 3$ $F_{CH} = 4n+6 = [C](3)+6(H) = C_3H_6$

k = 3

CCG-2-Skeletal shape

k = 3

CCG-2- Hydrocarbon

k = 3

M-2: k = 1,2,3, 4

M-2:

k = 1   k = 2   k = 3   k = 4

M-3: k = 2, 3, 4

M-3:

4n+8   4n+6   4n+6

4n+4

M-4: k = 3, 4, 5, 6

k = 3   4n+10   k = 4   4n+8

M———M———M———M   M———M———M═══M

M-4   4n+8   4n+6   4n+4

Scheme 2. Possible skeletal shapes M-2, M-3 and M-4 clusters

4n+2   4n+4   4n+6   4n+6

k = 9   k =8   k =7   k = 7

4n+12   4n+10   4n+8

M———M———M———M———M

k =4   k = 5   k = 6

Scheme 3. Possible skeletal shapes of M-5 cluster systems

CCG-3: $SeFe_3(CO)_9(CuCl)^{2-}$
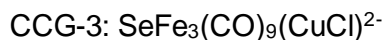
$1[Se] \longrightarrow 1[6] = 1[4+2] \longrightarrow 4n+2(n=1)$

$3[Fe(CO)_3] \longrightarrow 3[14+0] \longrightarrow 3[14+0-10]=3[4+0] \longrightarrow 4n+0(n=3)$

$1[CuCl(CO)] \longrightarrow 1[14+0] \longrightarrow 1[14+0-10] =1[4+0] \longrightarrow 4n+0(n=1)$

$[9-9-1](CO) = -1(CO) \longrightarrow 0-2(n=0)$

$q \longrightarrow 0+2(n=0) \quad q = charge$

$S = 4n+2(n=5)$

$k = 2n-1 =2(5)-1 = 9$

$F_{CH} = 4n+2 = [C](5)+2(H) = C_5H_2 = B_5H_5{}^{2-}$ This is a closo cluster and is expected to have a shape similar to that of $B_5H_5{}^{2-}$, trigonal bipyramid.

$S = 4n+2$

$k =9$
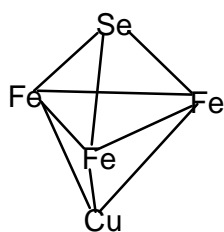
C_5H_2

Mapping skeletal structure of C_5H_2 will be the same as in F-12.

CCG-3

CCG-4: $TeRu_5(CO)_{14}{}^{2-}$

$S = 4n+2$, (n=6), closo cluster

$F_{CH} = C_6H_2, \quad F_B = B_6H_6{}^{2-}$

Octahedral shape expected.
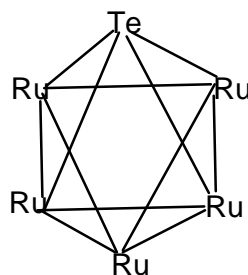
CCG-4. Observed skeletal shape

The C_6H_2 hydrocarbon can be mapped onto an octahedral geometry as in F-13.

CCG-5: $TeRu_5(CO)_{14}(CuCl)_2^{2-}$

$$1[Te] \longrightarrow 1[4+2] \longrightarrow 4n+2(n=1)$$

$$5[Ru(CO)_3] \longrightarrow 5[14+0] \longrightarrow 5[14+0-10]=5[4+0] \longrightarrow 4n+0(n=5)$$

$$2[CuCl(CO)] \longrightarrow 2[14+0] \longrightarrow 2[14+0-10]=2[4+0] \longrightarrow 4n+0(n=2)$$

$$[14-15-2](CO) \longrightarrow -3(CO) \longrightarrow 0-6(n=0)$$

$$q \longrightarrow 0+2(n=0)$$
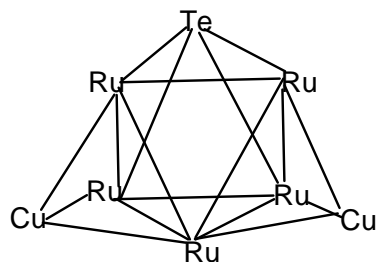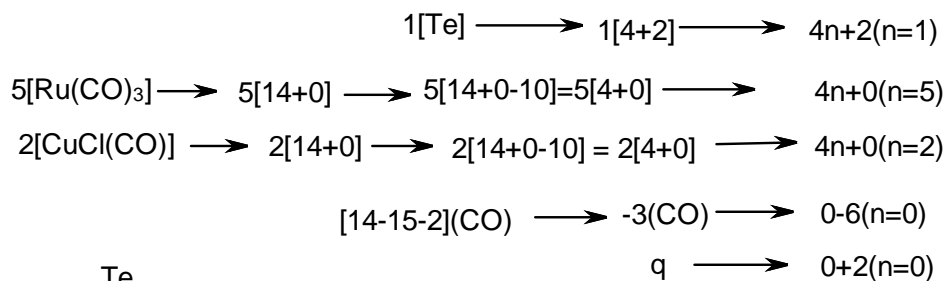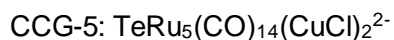
Bi-capped closo cluster

$Cp = C^2C[M-6]$

$$S = 4n-2(n=8) \qquad F_C = C_8^{2+}$$

This means 2 skeletal atoms are capped onto an octahedral geometry.

CCG-5. Observed skeletal shape
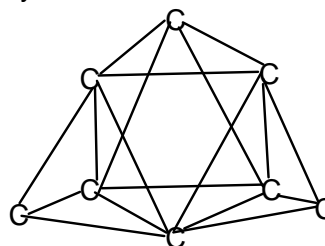
Possible hypothetical skeletal sketch of C_8^{2+} ion

Table 1. Carbonyl chalcogenide clusters and their hydrocarbon analogues

Cluster	Series	n	Hydrocarbon	k value
$Cr_2(Cp)_2(CO)_6$	4n+6	2	C_2H_6	1
$SeCr_2(Cp)_2(CO)_4$	4n+4	3	C_3H_4	4
$Se_2Cr(Cp)(CO)_2^-$	4n+6	3	C_3H_6	3
$TeCr_2(CO)_{10}^{2-}$	4n+8	3	C_3H_8	2
$SeFe_3(CO)_9^{2-}$	4n+4	4	C_4H_4	6
$SeCr_3(CO)_6(Cp)_3^-$	4n+6	4	C_4H_6	5
$TeCr_3(CO)_{15}^{2-}$	4n+10	4	C_4H_{10}	3
$Se_2Cr_3(CO)_{10}^{2-}$	4n+2	5	C_5H_2	9
$Se_2Cr_3(CO)_{16}^{2-}$	4n+2	5	C_5H_2	9
$Se_2Mn_3(CO)_9$	4n+2	5	C_5H_2	9
$SeFe_3(CO)_9(CuCl)^{2-}$	4n+4	5	C_5H_4	8
$Te_4Cr(CO)_4^{2-}$	4n+10	5	C_5H_{10}	5
$SeFe_3(CO)_9(CuCl)_2^{2-}$	4n+0	6	C_6	12
$TeRu_5(CO)_{14}^{2-}$	4n+2	6	C_6H_2	11
$Te_2Cr_4(CO)_{18}^{2-}$	4n+10	6	C_6H_{10}	7
$Re_6H_5(CO)_2^{4-}$	4n+12	6	C_6H_{12}	6
$Te_2Cr_4(CO)_{20}^{2-}$	4n+14	6	C_6H_{14}	5
$TeRu_5(CO)_{14}(CuCl)_2^{2-}$	4n-2	8	C_8^{2+}	17
$CH_2Te_2Cr_6(CO)_{30}^{2-}$	4n+20	9	C_9H_{20}	8

Table 2. Hydrocarbons and carbon clusters arranged according to the number of skeletal carbon atoms

M-1	CH_4	CH_2	C	C^{2+}										
M-2	C_2H_6	C_2H_4	C_2H_2	C_2	C_2^{2+}									
M-3	C_3H_8	C_3H_6	C_3H_4	C_3H_2	C_3	C_3^{2+}								
M-4	C_4H_{10}	C_4H_8	C_4H_6	C_4H_4	C_4H_2	C_4	C_4^{2+}							
M-5	C_5H_{12}	C_5H_{10}	C_5H_8	C_5H_6	C_5H_4	C_5H_2	C_5	C_5^{2+}						
M-6	C_6H_{14}	C_6H_{12}	C_6H_{10}	C_6H_8	C_6H_6	C_6H_4	C_6H_2	C_6	C_6^{2+}					
M-7	C_7H_{16}	C_7H_{14}	C_7H_{12}	C_7H_{10}	C_7H_8	C_7H_6	C_7H_4	C_7H_2	C_7	C_7^{2+}				
M-8	C_8H_{18}	C_8H_{16}	C_8H_{14}	C_8H_{12}	C_8H_{10}	C_8H_8	C_8H_6	C_8H_4	C_8H_2	C_8	C_8^{2}			
M-9	C_9H_{20}	C_9H_{18}	C_9H_{16}	C_9H_{14}	C_9H_{12}	C_9H_{10}	C_9H_8	C_9H_6	C_9H_4	C_9H_2	C_9	C_9^{2+}		
M-10	$C_{10}H_{22}$	$C_{10}H_{20}$	$C_{10}H_{18}$	$C_{10}H_{16}$	$C_{10}H_{14}$	$C_{10}H_{12}$	$C_{10}H_{10}$	$C_{10}H_8$	$C_{10}H_6$	$C_{10}H_4$	$C_{10}H_2$	C_{10}	C_{10}^{2+}	
M-11	$C_{11}H_{24}$	$C_{11}H_{22}$	$C_{11}H_{20}$	$C_{11}H_{18}$	$C_{11}H_{16}$	$C_{11}H_{14}$	$C_{11}H_{12}$	$C_{11}H_{10}$	$C_{11}H_8$	$C_{11}H_6$	$C_{11}H_4$	$C_{11}H_2$	C_{11} C_{11}^{2+}	
M-12	$C_{12}H_{26}$	$C_{12}H_{24}$	$C_{12}H_{22}$	$C_{12}H_{20}$	$C_{12}H_{18}$	$C_{12}H_{16}$	$C_{12}H_{14}$	$C_{12}H_{12}$	$C_{12}H_{10}$	$C_{12}H_8$	$C_{12}H_6$	$C_{12}H_4$	$C_{12}H_2$ C_{12} C_{12}^{2+}	

Table 3. Hydrocarbon clusters arranged according to series

	Bicp	Monocp	Closo	Nido	Arachno	Hypho	Klapo				
	4n-2	4n+0	4n+2	4n+4	4n+6	4n+8	4n+10	4n+12	4n+14	4n+16	4n+18
M-1	C^{2+}	C	CH_2	CH_4							
M-2	C_2^{2+}	C_2	C_2H_2	C_2H_4	C_2H_6						
M-3	C_3^{2+}	C_3	C_3H_2	C_3H_4	C_3H_6	C_3H_8					
M-4	C_4^{2+}	C_4	C_4H_2	C_4H_4	C_4H_6	C_4H_8	C_4H_{10}				
M-5	C_5^{2+}	C_5	C_5H_2	C_5H_4	C_5H_6	C_5H_8	C_5H_{10}	C_5H_{12}			
M-6	C_6^{2+}	C_6	C_6H_2	C_6H_4	C_6H_6	C_6H_8	C_6H_{10}	C_6H_{12}	C_6H_{14}		
M-7	C_7^{2+}	C_7	C_7H_2	C_7H_4	C_7H_6	C_7H_8	C_7H_{10}	C_7H_{12}	C_7H_{14}	C_7H_{16}	
M-8	C_8^{2}	C_8	C_8H_2	C_8H_4	C_8H_6	C_8H_8	C_8H_{10}	C_8H_{12}	C_8H_{14}	C_8H_{16}	C_8H_{18}
M-9	C_9^{2+}	C_9	C_9H_2	C_9H_4	C_9H_6	C_9H_8	C_9H_{10}	C_9H_{12}	C_9H_{14}	C_9H_{16}	C_9H_{18}
M-10	C_{10}^{2+}	C_{10}	$C_{10}H_2$	$C_{10}H_4$	$C_{10}H_6$	$C_{10}H_8$	$C_{10}H_{10}$	$C_{10}H_{12}$	$C_{10}H_{14}$	$C_{10}H_{16}$	$C_{10}H_{18}$
M-11	C_{11}^{2+}	C_{11}	$C_{11}H_2$	$C_{11}H_4$	$C_{11}H_6$	$C_{11}H_8$	$C_{11}H_{10}$	$C_{11}H_{12}$	$C_{11}H_{14}$	$C_{11}H_{16}$	$C_{11}H_{18}$
M-12	C_{12}^{2+}	C_{12}	$C_{12}H_2$	$C_{12}H_4$	$C_{12}H_6$	$C_{12}H_8$	$C_{12}H_{10}$	$C_{12}H_{12}$	$C_{12}H_{14}$	$C_{12}H_{16}$	$C_{12}H_{18}$

Table 4. The k values of hydrocarbon clusters

	Bicp	k_{bicp}	Monocp	Closo	Nido	Arachno	Hypho	Klapo				
	4n-2	2n+1	4n+0	4n+2	4n+4	4n+6	4n+8	4n+10	4n+12	4n+14	4n+16	4n+18
M-1	C^{2+}	**3**	2	1	0							
M-2	C_2^{2+}	**5**	4	3	2	1						
M-3	C_3^{2+}	**7**	6	5	4	3	2					
M-4	C_4^{2+}	**9**	8	7	6	5	4	3				
M-5	C_5^{2+}	**11**	10	9	8	7	6	5	4			
M-6	C_6^{2+}	**13**	12	11	10	9	8	7	6	5		
M-7	C_7^{2+}	**15**	14	13	12	11	10	9	8	7	6	
M-8	C_8^{2}	**17**	16	15	14	13	12	11	10	9	8	7
M-9	C_9^{2+}	**19**	18	17	16	15	14	13	12	11	10	9
M-10	C_{10}^{2+}	**21**	20	19	18	17	16	15	14	13	12	11
M-11	C_{11}^{2+}	**23**	22	21	20	19	18	17	16	15	14	13
M-12	C_{12}^{2+}	**25**	24	23	21	20	19	18	17	16	15	14

3. Conclusion

The sample of carbonyl chalcogenide complexes that were investigated portrayed a tendency of being dominated by clusters that structurally behave like hydrocarbons. The introduction of copper (group 11) seems to induce capping into the clusters as deduced by 4n series method. If n<q, in the hydrocarbon C_nH_q there is a tendency for a cluster fragment to structurally behave as its equivalent hydrocarbon. If n = q, then a borderline case appears to be attained. On the other hand if n>q, the clustering tendency appears to increase. When q=0, then S = 4n+0, we get carbon series C_n(n =1, 2,3,..) which belong to the clan of mono-capped series. Different clusters can be transformed into hydrocarbons. Such hydrocarbons may be used as model clusters. The 4n series may be viewed as a unifier of many different clusters and as a mirror for seeing special features in atoms, molecules, fragments and clusters.

Acknowledgements

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