M·Sc Semester-II, Paper: CC-06 (Inorganic chem)

Unit: 5 Metal-carbonyl clusters. [By Dr. Birendra Kumar, Maharaja College]

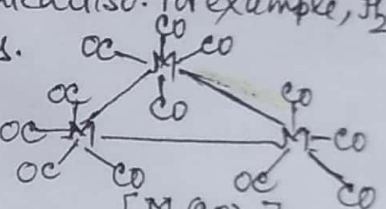
When a number of metal carbonyl (homo or hetero) molecules grow closely together, metal-carbonyl cluster formed. Metal carbonyl clusters range in size from dinuclear to a very high nuclearity (20 or more metal atoms). The metal carbonyl clusters may be homo or heterotype. When metal-carbonyl clusters contain one metal, they are homo-type, e.g. $Os_3(CO)_{12}$. Metal-carbonyl clusters containing different metals are referred as heterotype or mixed metal clusters, e.g. $H_2FeRu_2Os(CO)_{13}$. Metal-carbonyl clusters commonly have intimate bound or even encapsulated non-metals (C, N, S, C etc.).

* Metal-carbonyl clusters are of two types:

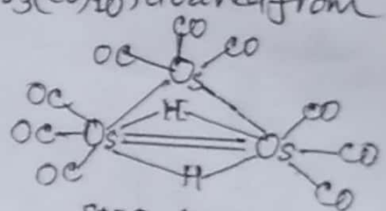
1. Low nuclearity carbonyl clusters 2. High nuclearity carbonyl clusters.

1. Low nuclearity carbonyl clusters: Metal carbonyl cluters containing 3 or 4 metal atoms are known as low nuclearity carbonyl clusters, e.g. $Ru_3(CO)_{12}$, $H_4Re_4(CO)_{12}$ etc. They are commonly prepared by pyrolysis method. Low nuclearity clusters may be triatomic, $M_3(CO)_{12}$ type or tetratomic, $M_4(CO)_{12}$ type.

(a) Triatomic carbonyl clusters: Linear triatomic clusters exist but are very less important, majority of these clusters are triangular, and heteronuclear. The triatomic clusters, $M_3(CO)_{12}$ are electronically saturated, i.e. metals possess 18 e closed shell configuration. In such system, there are 48 electrons and each metal-metal bond is of order one. However, some clusters are unsaturated also. For example, $H_2Os_3(CO)_{10}$, derived from $Os_3(CO)_{12}$, possessing total 46 electrons.



$[M_3(CO)_{12}]$

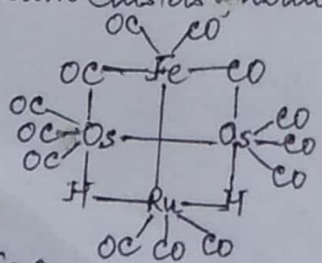


$[H_2Os_3(CO)_{10}]$

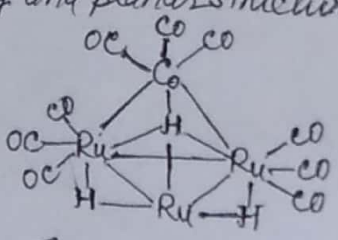
$Ru_3(CO)_{12}$ & $Os(CO)_{12}$ clusters are unreactive to some extent. They can be converted into more reactive derivatives by replacement of one or two CO (ligand) / reaction with H_2 under pressure.

(b) Tetratomic carbonyl clusters: Tetratomic carbonyl clusters are mostly hetero nuclear / hetero form. They are generally prepared by pyrolysis method. Majority of them possess tetrahedral structure and derived from $M_4(CO)_{12}$ (where M = Co, Rh & Ir). In these, the 18e rule is satisfied for each metal atom through the formation of six metal-metal single bond and total number of electrons is 60.

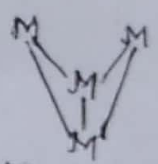
The compound $H_4Re_4(CO)_{12}$ has only 56 electrons but has a regular tetrahedral core of Re_4. The existence of discrete, localized Re-Re double bonds, both resonating double bonds or the formation of three centre bonding have been established. Four atom clusters with butterfly and planar structures also possessed by these clusters.



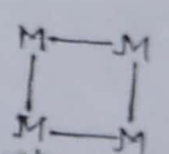
$[H_2Os_2RuFe(CO)_{13}]$



$[H_3Ru_3Co(CO)_9]$



(Butterfly Structure) (62e System)



(Square Planar Structure) (64e System)

2. High nuclearity clusters: Metal-carbonyl clusters having five or more metal atoms, each forming at least one metal-metal bond are known as high nuclearity clusters. e.g., $[Os_6(CO)_{18}]^{2-}$, $[Rh_6(CO)_{16}]$, $[H_2Ru_6(CO)_{18}]$ etc. In some of these (close polyhedra), a heteroatom such as C, H, O, N may be encapsulated, e.g. $[Co_6(CO)_{15}H]$, other less common polyhedra are the trigonal bipyramidal found in $[Ni_5(CO)_{12}]^{2-}$, $[Ni_3Mo_2(CO)_{13}]$ & $[Os_5(CO)_{16}]$, trigonally distorted octahedron as in $[Ni_6(CO)_{12}]$. Close packed arrays in which the metal atoms are grouped much as they are in bulk metal. Rh & Pt provide many examples of these. Stacked triangular arrays as in the $[Ni_3(CO)_6]_n^{2-}$ ($n = 2$ to 5) species and similar Pt-ones.

⇒ Total electron count (TEC): This is more elaborate and differently derived treatment/parameter used for structure prediction of large clusters. The TEC (total electron count) is obtained from the formula by adding the following contributions:
(i) The number of valence electrons for each metal atom. For example in an Os_6-cluster $6 \times 8 = 48$.
(ii) Two electrons for each CO (ligand) (iii) one electron for each -ve charge.
(iv) The number of valence electrons for each hetero and interstitial atom. For example, one for H, four for carbon, five for phosphorus/nitrogen.

* Calculation of TEC & Prediction of the structure of clusters:

For metal-carbonyl clusters, it is assumed that in addition to the electrons necessary for skeletal bonding, each metal atom will also have 12 non-skeletal electrons. The basis for this assumption is that the pyramidal $M(CO)_3$ unit, each M-CO bond will contain two formally 'carbon-σ' electrons that are donated to the metal atom and two formally 'metal π' electrons that back bonded to CO ligand. Thus, in predicting the TEC for a 'closo' polyhedral cluster of n vertices, the result would be $[12n + 12(n+1)]$. For 'nido' & 'arachno' clusters that are derived from an n-vertex polyhedron by removal of one or two vertices respectively, there will be 12 & 24 fewer total electrons respectively. The predictions for TEC can be stated in the following relations:

Closo: $[12n+2(n+1)]$; nido: $[12(n-1)+2(n+1)]$; arachano: $[12(n-2)+2(n+1)]$
(where n = number of vertices in the parent polyhedron for the nido & arachno cases.)

For example, TEC of $[Rh_6(CO)_{16}] = (9 \times 6) + (2 \times 16) = 86$. The number of skeletal pairs (S) will be obtained by substracting 6×12, i.e. 72 from 86 and dividing by 2. The result is 7. Since the number of vertices of the parent polyhedron is (S-1). We conclude that this will be six vertex polyhedron, i.e, an octahedron. Since there are 6 metal atoms, we find a 'closo' structure, and an octahedron is suitable structure.

In general, 86 electrons clusters containing 6 metal atoms are octahedral structure.

Another example is $[Os_5(CO)_{16}]$ cluster which has a closo structure can be predicted in a similar manner. $[Os_5C(CO)_{15}]$ & $[Fe_4C(CO)_{15}]$ show 'nido' & 'arachno' structures respectively. The nido structure for the iron analogue $[Fe_4C(CO)_{15}]$ is derived by removal of one vertex from the parent polyhedron, which is an octahedral structure of geometry. The $[Fe_4C(CO)_{12}]$ cluster should be isostructural with the $[Fe_4C(CO)_{13}]$ cluster. It is derived from a parent octahedron by removal of two vertices. A tetrahedron is treated as a trigonal bipyramid that is missing one vertex, i.e, a nido structure.