Class – P.G. Sem(II)
Subject – Inorganic chemistry
Paper – CC–VI
Unit – IV

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INORGANIC CHAINS, RINGS, CAGES AND CLUSTERS:-III

Metal Clusters :-

A metal cluster is a group of two or more metal atoms that are directly linked with one another through metal-metal bond. Calomel was the first known by Indian chemist in which Hg – Hg bond is present. The metal clusters are divided into two categories:

1. Carbonyl clusters and
2. Halide type clusters.

1. Carbonyl clusters – In carbonyl cluster the oxidation number of metal is low (-1, 0 and +1) and the nature of d- orbital or the mainly with the last few members of 1st, IInd and IIIrd transition metal series. It includes neutral carbonyls, carbonyl anions and hydrido carbonyls. Such compounds are related with each other in which on CO group can be replaced by two H-atoms or by one H atom and one negative charge. The carbonyl clusters are

divided into two groups:

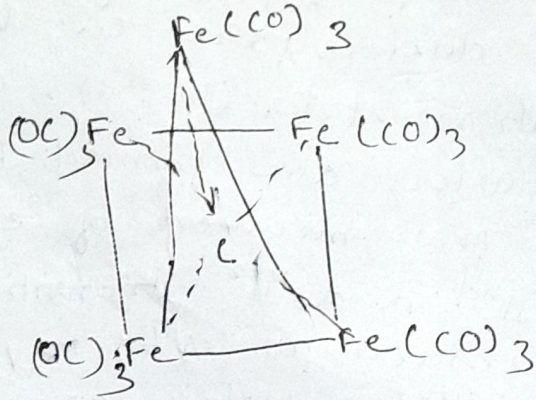
(a) Low Nuclearity carbonyl clusters (LNCC)

(b) High Nuclearity carbonyl clusters (HNCC)

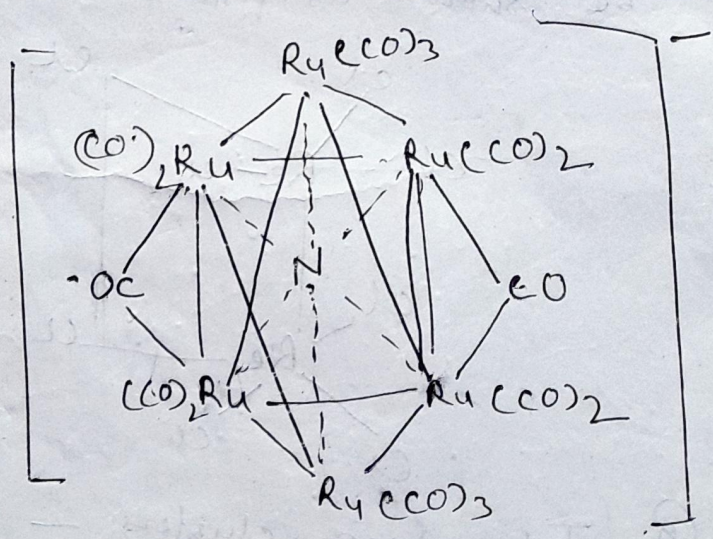
(a) LNCC or low nuclearity carbonyl clusters — They are the carbonyls in which number of metal atoms is small i.e 2, 3 or 4. These are also known as di, tri or tetra-nuclear carbonyl clusters respectively.

(b) High Nuclearity carbonyl clusters or HNCC — They are the carbonyls in which number of metal atoms is five or more than five which are bonded directly with one another, eg $Rh_6(CO)_{16}$ $Ru_6(CO)_6H_2$ and $[Ni_3(CO)_6]_n^{2-}$. Some mixed carbonyl clusters containing carbon atoms are also known. These are known as carbido carbonyl clusters. These may be prepared either by pyrolysis or by refluxing metal carbonyls with $CHCl_3$, CCl_4 etc solvent. For example $Fe_5C(CO)_{15}$, $Ru_6C(CO)_{17}$, $[Os_{10}C(CO)_{24}]^-$ and $FeC(CO)_{13}$.

structure of $Fe_6C(CO)_{15}$ is

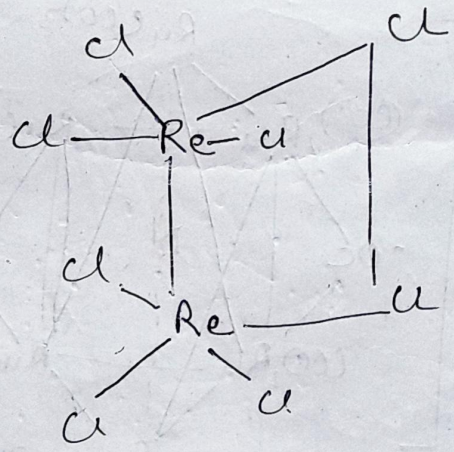


Many nitrido carbonyl clusters are also known in which nitrogen atoms is encapsulated in the structure. The structure of $[Ru_6N(CO)_{16}]^-$ is given below —



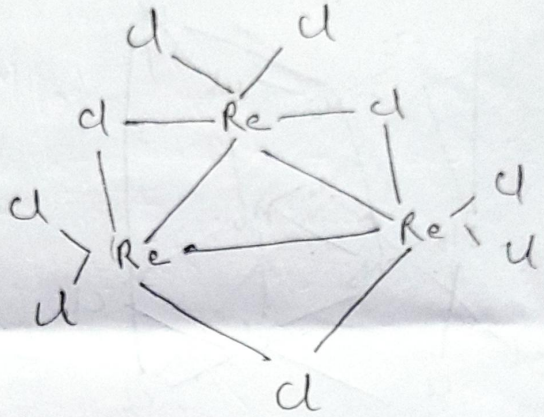
(2) Halide type clusters — In halide type clusters metal atoms are in higher oxidation states (+2, +3). Such type of clusters are formed by the first few members of each of the IInd and IIIrd transition metal series such as Nb, Ta, W, Re. The halide clusters are different types depending on the number of metal atoms. They are:

(1) Di-nuclear clusters — The best example of this type of clusters are $[Re_2X_8]^{2-}$ ions (X = Cl, Br, I, NCS etc.) The structure of $[Re_2Cl_8]^{2-}$ ion may be shown as follows:



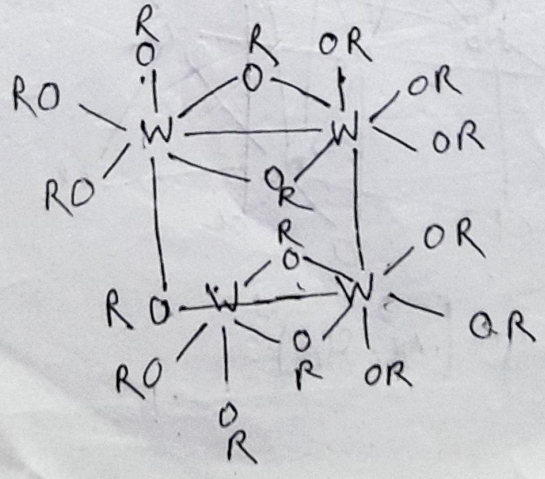
(2) Trinuclear clusters — The best known example of this type is R_3X_9 where X = Cl, Br, I. In this cluster the oxidation state of Re = +3 with configuration $5d^4$. Each Re atom in the triangular

array is coordinated by two more Cl^- ligands above and below the plane. If we assume that Re-Re single bond is present, the molecule should be paramagnetic, while it is diamagnetic it indicate that Re-atom is doubly bonded to its neighbour Re-atom.



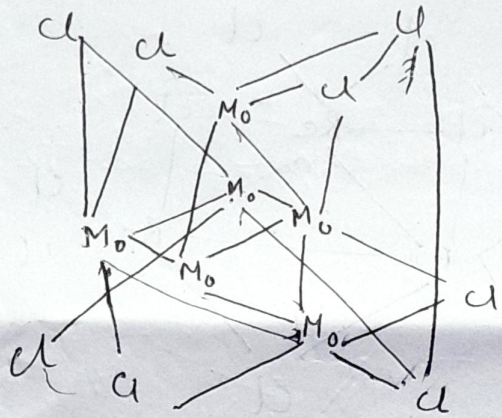
Re_3Cl_9.

(iii) Tetranuclear clusters — The dimer of dinuclear alkoxide of $W_2(OR)_6$ form tetranuclear metal cluster $W_4(OR)_{12}$. Structure of $W_4(OR)_{16}$ is given below:—

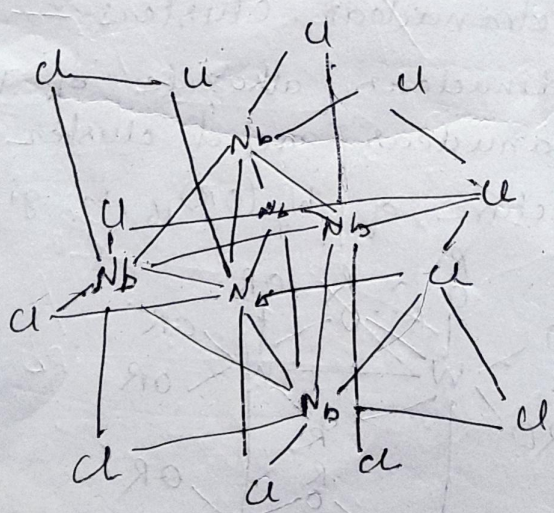


$W_4(OR)_{16}$

(IV) Hexanuclear clusters — The metals such as Mo, W, Nb and Ta form such type of clusters. These clusters are of two types (i) $M_6X_8^{4+}$ and (ii) $M_6X_{12}^{2+}$. In both types metal atoms forms octahedral geometry. Structure of $[Mo_6Cl_8]^{4+}$ and $[Nb_6Cl_{12}]^{2+}$ are shown below —



$[Mo_6Cl_8]^{4+}$



$[Nb_6Cl_{12}]^{2+}$

Apart from metal clusters of carbonyl and halide there are new two types of metal clusters are recently discovered they are cheveral phase and Zintl ions.

Chevrel phase are mixed Mo clusters, its general formula is $M_x Mo_6 X_8$ where M = Pb, Sn, Cu, cd, Fe and X = S, Se, Te, Such clusters have both unusual structures and interesting electrical and magnetic properties Since Roger chevrel discovered such clusters hence these are named as Chevrel phase.

Zintl ions are also known as Naked clusters or clusters without ligands. The Polyatomic cations cations are stabilized by weakly basic anions such as $AlCl_4^-$. e.g

$$4Bi + BCl_3 + 3AlCl_3 \text{(excess)} \rightarrow Bi_5[AlCl_4]_3$$

Such homo poly atomic ions are known as zintl ions.