

Metal clusters: —

Compounds containing metal-metal bonds are called metal cluster compounds. Metal-metal bond containing compounds were known to the chemists of India as early as twelfth century.

Metal clusters are classified in two groups

- Polynuclear carbonyls, nitrosyls and related compounds
- Halide and oxide compounds.

Metal atoms in class-I have low formal oxidation states -1 to $+1$ while those of class-II are found in higher formal oxidation states ($+2$ to $+3$)

The transition metals on the right side of the periodic table (the late transition metals) typically form class-I ~~comp~~ cluster compounds, while early 2nd and 3rd transition metals tend to form class-II clusters.

⇒ Generally, the metals that have large energies of atomization are more likely to form clusters.

Thus the most refractory metal (Zr, Nb, Mo, Tc, Ru, Rh, Hf, Ta, W, Re, Os, Ir & Pt) have greatest tendency to form metal clusters.

⇒ The second factor for the cluster formation is the nature of d orbitals — the size of d orbital is inversely related to the effective nuclear charge. Effective overlap of d orbitals are necessary to stabilise the metal clusters.

Thus excessive contraction of d orbital will

destabilise the metal clusters, i.e., high oxidation states are unfavourable for cluster formation.

⇒ For the 1st transition series, d orbitals are relatively small, and even in moderately low oxidation states ($+2$ & $+3$) disfavour the cluster formation.

Class-I clusters: —

Dinuclear class-I clusters: —

(i) $Mn_2(CO)_{10}$ is the simplest dinuclear carbonyl compounds without any bridging CO molecule

(ii) $Co_2(CO)_8$, has two bridging CO in solid state but no bridging CO in solution.

(iii) Other dinuclear carbonyl compounds include, $Re_2(CO)_{10}$, $Tc_2(CO)_{10}$, $Fe_2(CO)_9$, $Ru_2(CO)_9$, $Os_2(CO)_9$. However among these $Fe_2(CO)_9$ is stable and others are less stable due to large metal-metal distance. $Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9$
 $Re_2O_7 + CO \xrightarrow[250^\circ C]{350 \text{ atm}} Re_2(CO)_{10}$

Trimuclear class-I clusters: — $Fe_3(CO)_{12}$ has both terminal & bridging CO, but $Os_3(CO)_{12}$ & $Ir_3(CO)_{12}$ have only terminal carbonyl. Though there are evidences that $Fe_3(CO)_{12}$ may exist in unbridged state and that depends on solvent i.e. in $mol \rightleftharpoons$

1st Transition Series → $Fe_3(CO)_{12}$

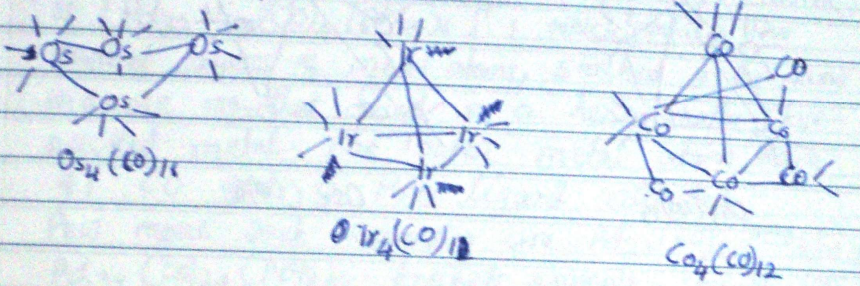
2nd " " → $Ru_3(CO)_{12}$

3rd " " → $Os_3(CO)_{12}$

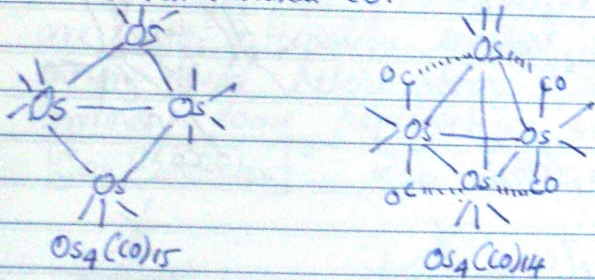
Q. what are the evidences in favour of CO-CO bond in $Co_2(CO)_8$?

Supernuclear Clusters

Tetranuclear class-I clusters: - well studied tetra-nuclear carbonyls are: $\rightarrow Os_4(CO)_{14}$, $Os_4(CO)_{15}$, $Os_4(CO)_{16}$, $Ir_4(CO)_{12}$, $Co_4(CO)_{12}$



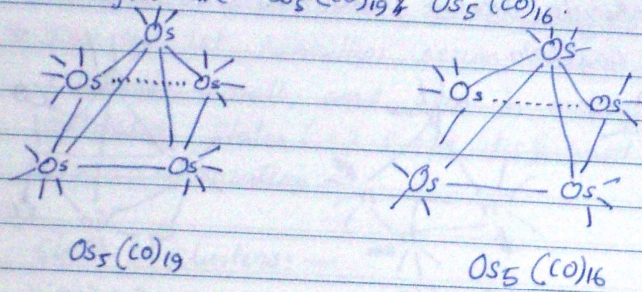
$Os_4(CO)_{16}$, $Os_4(CO)_{15}$ and $Os_4(CO)_{14}$ has, 4, 5 & 6 metal-metal bonds. In $Os_4(CO)_{14}$ has 4 semi-bridging CO and four terminal CO.



$Os_4(CO)_{15}$ has planar Os_4 unit with only nonbridged CO.

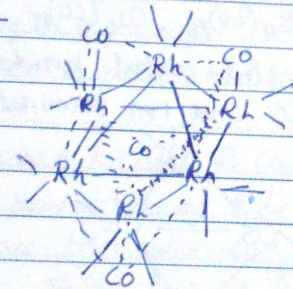
Q. $Co_4(CO)_{12}$ has bridged CO ligand but $Ir_4(CO)_{12}$ does not. Why?

Pentanuclear class-I clusters: - Important penta nuclear carbonyls are $Os_5(CO)_{19}$ & $Os_5(CO)_{16}$.



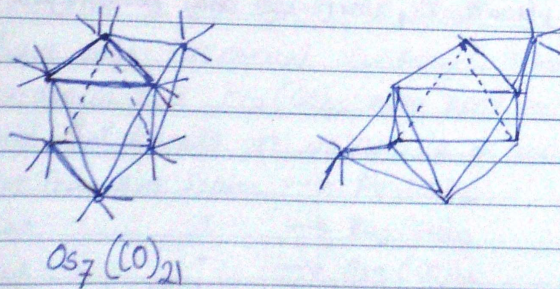
Hexanuclear class-I clusters: -

$Co_6(CO)_{16}$
 $Rh_6(CO)_{16}$
 $Os_6(CO)_{18}$ & $Os_6(CO)_{21}$



Hepta $\rightarrow Os_7(CO)_{21}$

Octa $\rightarrow Os_8(CO)_{23}$



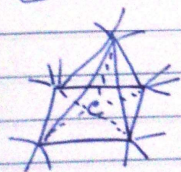
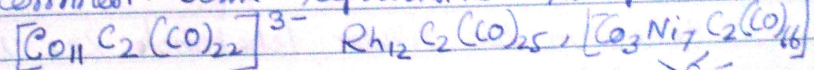
Superlarge clusters:—

Many large clusters have reported that their internal structures are very much metal like. An important example of such superlarge cluster is $[Pd_{33}Ni_9(CO)_{41}(PPh_3)_6]^{4-}$, which contains five central layers of metal atoms, stacked in the same manner as that found in a hexagonally close-packed metal. The outer metal atoms have 41 CO and 6 PPh_3 ligand attached.

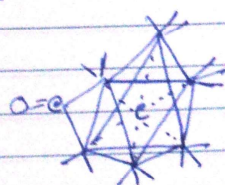
Few more such examples are $Pd_{23}(CO)_{22}(PET_3)_{10}$ & $Pd_{34}(CO)_{24}(PET_3)_{12}$. Another example is $[Au_6Ni_{12}(CO)_{24}]^{2-}$

Hetero atoms in clusters:—

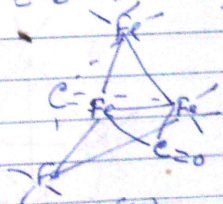
Nonmetal atoms like C, H, N, P, As & S are also intimately involved in metal clusters. Among these hetero atoms N & C is very common. Some representative examples are:



$Fe_5C(CO)_{15}$

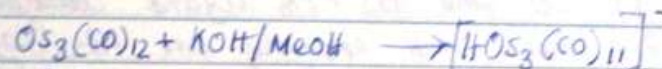
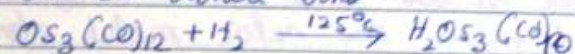


$Ru_6C(CO)_{17}$

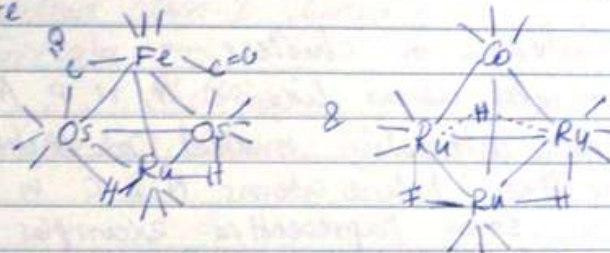


$Fe_4C(CO)_{13}$

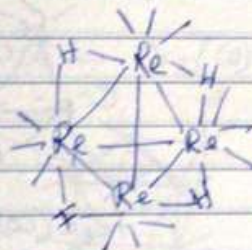
Few more important hetero atom containing clusters are $H_2Os_3(CO)_{10}$ which is derived from $Os_3(CO)_{12}$. In this cluster one Os-Os is shorter than other (2.68 Å compared to 2.88 Å) and, bridged by hydrogen atom and there is one Os=Os double bond.



Some hetero nuclear hydrogen containing clusters are



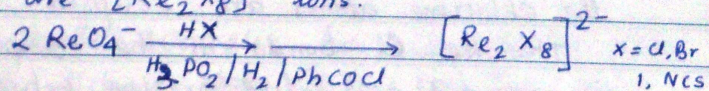
$H_4Re(CO)_{12}$ has regular tetrahedral Re_4 unit



Clusters

Clam-II metal clusters:-

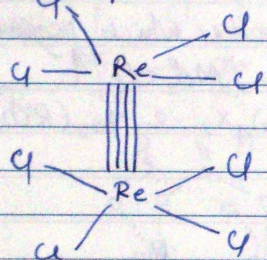
Dinuclear metal cluster:- Best studied binuclear species are $[Re_2X_8]^{2-}$ ions.



Features: (1) Unusual Re-Re distance 224 pm compared to 275 pm of Re metal.

(ii) eclipsed configuration of chlorine atoms.

Cotton explained both phenomena by invoking a quadruple bond.



structure elucidation:-

(a) each Re atom is dsp^2 hybridised and form 4 Re-Cl bonds

(b) The metal d_{z^2} & p_z lie along z-axis and may be hybridised to form one

orbital directed toward other Re atom and second orbital directed opposite direction.

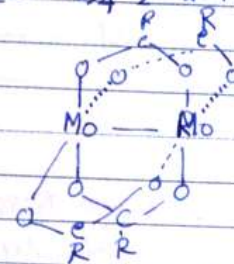
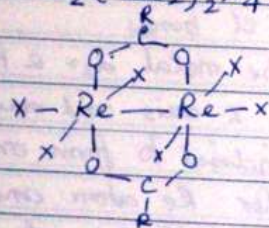
The former can overlap with similar orbital and form a σ bond, while second hybrid orbital forms an approximately non-bonding orbital.

The d_{xz} and d_{yz} of each Re atoms overlap to form π bonds. A fourth bond can now form by 'side ways' overlap of

the remaining d_{xy} orbital on each Re atoms. Overlap of d_{xy} orbitals can only occur if the chlorine atoms are eclipsed.

The Re-Cl bonds in the complex may be regarded as dative overlap between Re^{3+} and Cl^- ligand and $Re^{3+} (d^4)$ ions. The eight d electrons from two Re ions will occupy the σ bonding, two π bonding and one δ bonding orbitals to form the quadruple bond.

There are many compounds which resemble the $[Re_2X_8]^{2-}$ ions like $[Mo_2Cl_8]^{4-}$, $Re_2(RCO_2)_2X_4$, $Re_2(RCO_2)_4X_2$ & $Mo_2(RCO_2)_4$:

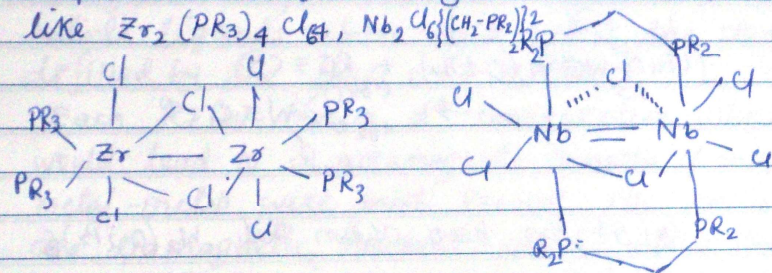


There are two metal ions in 1st transition series which form acetate complexes; Cu & Co complexes are diamagnetic and spins are paired. The Cu-Cu distance in Cu(II) acetate complex is 264 pm longer than Cu-Cu distance in metallic copper, indicating Cu-Cu bond in Cu(II) acetate

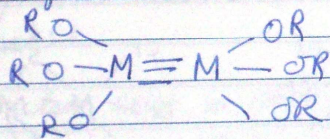
is only a weak single bond resulting from pairing the odd electron on each copper atom.

Cr(II) acetate complex has considerable shorter Cr-Cr distance ~~than~~ (236.2 pm) than Cr-Cr bond in metallic chromium.

a) There are many complexes in the binuclear complexes with edge sharing octahedra like $Zr_2(PR_3)_4Cl_4$, $Nb_2Cl_6(CH_2-PR_2)_2$

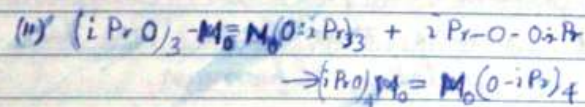
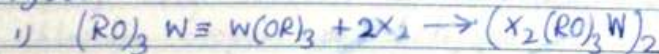


(b) Metal-metal multiple bonded complexes also includes hexaalkoxo dinuclear tungsten & Molybdenum complexes of $M_2(O)_6$

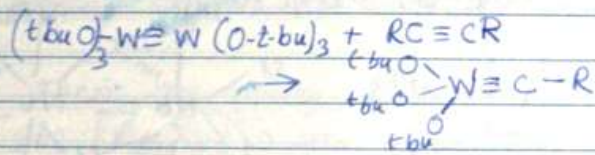


This metal-metal triple bond is somewhat analogous to $C \equiv C$ triple bond, and triple bond formation occur due to one sigma

and two π bonding ($\sigma^2 \pi^4$). This bond undergoes:-

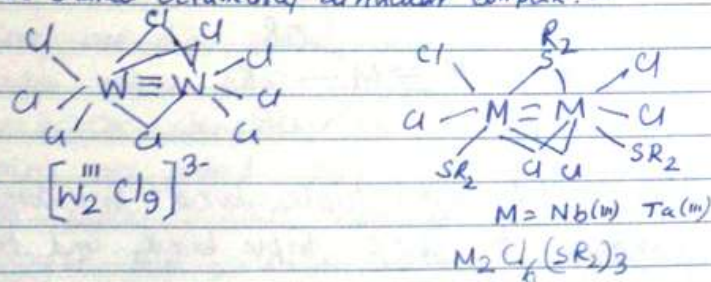


(iii) It is also possible to prepare $(t-buO)_3 W \equiv CR$



(iv) It has been shown that $W_2(O-iPr)_6$ dimerizes and exist in equilibrium with $W_4(O-iPr)_{12}$; a molecule which may be thought of an atat analogue of cyclobutadiene.

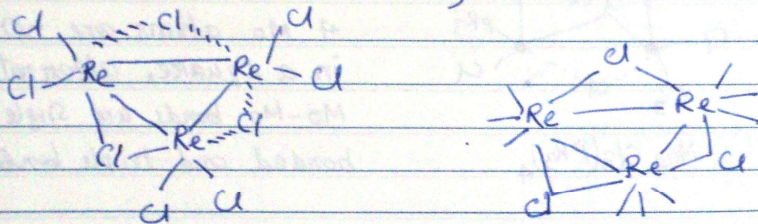
Face shared octahedral dinuclear complex:-



Tri nuclear metal cluster: →

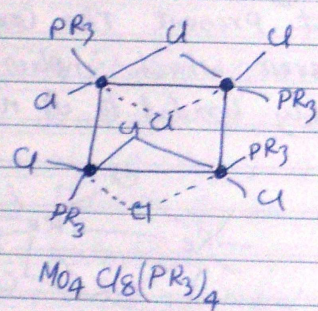
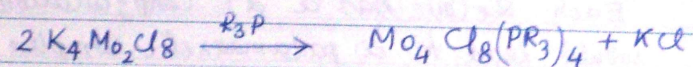
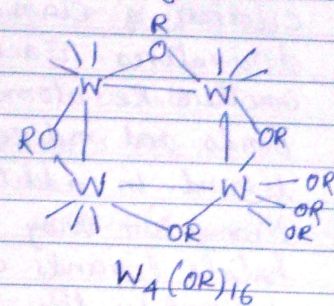
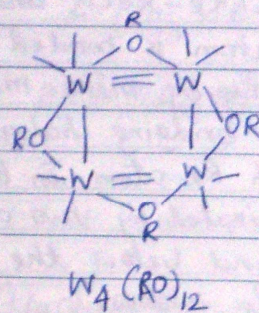
Best known example of trinuclear metal cluster of class -II is $\text{Cl}_3\text{Re}-\text{ReCl}_3$ and its derivatives. Each Re atom is bonded to the another Re atoms directly by metal-metal bonds and indirectly by bridging halogen ligand. In addition each Re atom in the triangular array is coordinated by two or more halide ligands above and below the plane defined by the three Re atoms.

Each Re(III) has a d^4 configuration, which would lead to a paramagnetic complex if only metal-metal were present. The complexes are diamagnetic, however, which implies that each Re atom is doubly bonded to its neighbours.



This structure exist in solid state only and dissolving the complex in a solution of the hydrochloric acid leads to formation of $(\text{Re}_3\text{Cl}_{12})^{3-}$

Tetranuclear cluster: - $\text{W}_4(\text{OR})_{12}$ which forms by dimerisation of $\text{W}_2(\text{OR})_6$ complex.

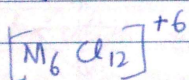
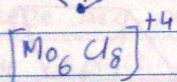
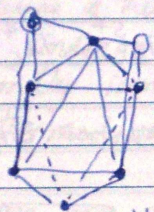
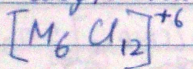


This molecular structure determination shows that 4 Mo atoms are not in a square, alternative Mo-Mo bonds are single bonded and triple bonded.

Hexanuclear complex: - Hexanuclear complexes adopt two classes of compound (1) An octahedron of six metal ligand atom is coordinated with 8 chloride ligands, one on each face of octahedron. This is found in Molybdenum dichloride $\text{Mo}_6\text{Cl}_{12}$

better formulated as $[Mo_6Cl_8]Cl_4$ i.e. $[Mo_6Cl_8]^{+4}$

(ii) This class also contains an octahedron of metal atoms but they are coordinated by 12 halide ligands along the edges. Nb(II) & Ta(II) adopts such structure of molecular formula



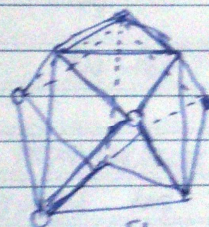
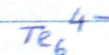
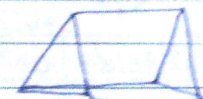
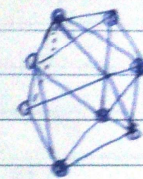
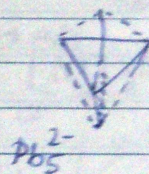
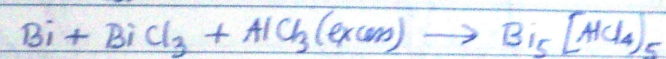
Reference:

Principle of Inorganic Chemistry, Huheey, Keiter, Keiter, Medi, 4th Edition,
Pearson Publication

Polyatomic Zintl anions & cations:—

Posttransition metals dissolved in liquid ammonia in presence of alkali metals gives highly coloured anions and their cryptate salt have been identified. These are mainly $[Na(crypt)_4]Pb_5$, $[Na(crypt)_4]Sn_9$ etc. Other anions are Pb_7^{2-} , Sb_7^{3-} , Bi_3^{3-} , Pb_5^{2-}

Polyatomic cations like Bi_5^{5+} , Te_6^{4+} are also obtained.



Since these homopolyatomic anions and cations are devoid of ligands they are also referred as naked clusters.

There is a good correlation between electronic structure and geometry as predicted by Wade's rule, though some exceptions are also known.