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METAL CLUSTERS

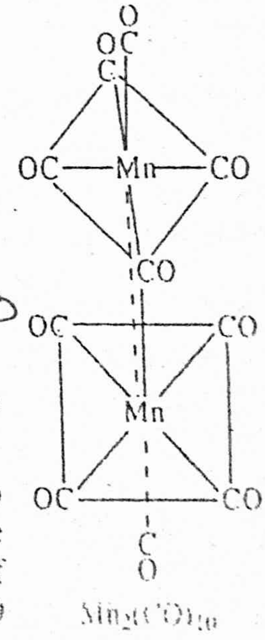
Metal Clusters. A metal cluster may be defined as a group of two or more metal atoms that are directly linked to one another through metal–metal bonds. Metal clusters can be broadly divided into two categories :

1. **Carbonyl clusters** in which the metal atoms are in low oxidation states (–1, 0, +1). The carbonyl groups in these clusters tend to stabilise the low oxidation states. Carbonyl clusters are formed mainly by the last few members of each of the First, Second and Third transition series, *viz.*, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt.

2. **Halide type of clusters** in which the metal atoms are in relatively higher oxidation states (+2, +3). These clusters are formed by the first few members of each of the Second and Third transition series, *viz.*, Nb, Ta, Mo, W, Re. Many clusters of this type contain multiple, *i.e.*, double and triple, metal–metal bonds.

1. CARBONYL CLUSTERS

The carbonyl clusters which we shall discuss here include neutral carbonyls, carbonyl anions and hydrido carbonyls. The relationship between the three types of carbonyls is based on the fact that one CO group can be replaced either by two H atoms or by one H atom and one negative charge or by two negative charges. The carbonyl clusters can be further subdivided into two categories, *viz.*, *(a) Low Nuclearity Carbonyl Clusters* (*LNCC*) and *(b) High Nuclearity Carbonyl Clusters* (*HNCC*).



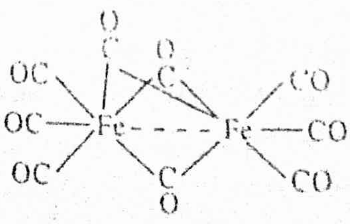
$Mn_2(CO)_{10}$
(I)

a. Low Nuclearity Carbonyl Clusters (LNCC). These clusters contain comparatively small number of metal atoms, *viz.*, 2, 3 or 4, in their structures. Accordingly we come across dinuclear, trinuclear and tetranuclear carbonyl clusters.

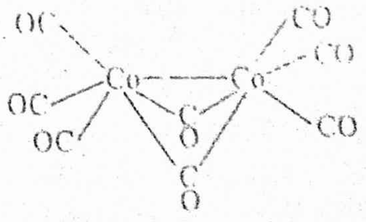
A number of **dinuclear carbonyl clusters** are known. Common examples are $Mn_2(CO)_{10}$, $Fe_2(CO)_9$ and $Co_2(CO)_8$.

In $Mn_2(CO)_{10}$, each metal atom has an octahedral environment and the two $Mn(CO)_5$ units are joined solely by Mn—Mn bond, as shown (Structure I). The carbonyl obeys the inert gas rule, each Mn atom having 36 electrons around itself ($25\,e^-$ from Mn + $1\,e^-$ from Mn–Mn bond + $2 \times 5 = 10\,e^-$ from five terminal CO groups = $36\,e^-$)

In the case of the carbonyl $Fe_2(CO)_9$, the two atoms of Fe are linked through three bridging carbonyl groups, as shown (Structure II). There are three terminal CO groups on each Fe atom. The carbonyl obeys the inert gas rule, each Fe atom having 36 electrons around itself ($26\,e^-$ from Fe + $3\,e^-$ from 3 bridging CO groups + $6\,e^-$ from 3 terminal CO groups + $1\,e^-$ from Fe–Fe bond). The dinuclear carbonyl $Co_2(CO)_8$ contains three terminal CO groups on each metal atom, two bridging carbonyl groups and a Co—Co bond in its structure, as shown (Structure III).

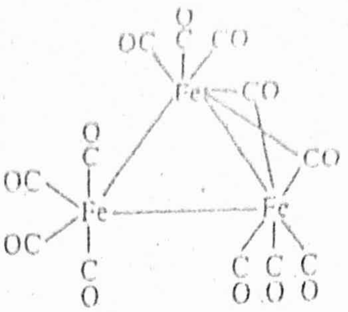


$Fe_2(CO)_9$
(II)



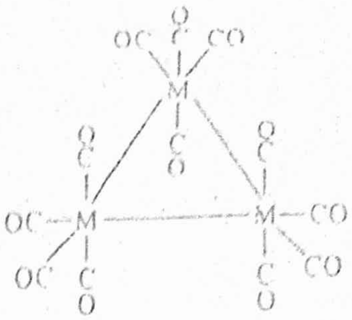
$Co_2(CO)_8$

The majority of M_3 clusters present in trinuclear carbonyls have a triangular geometry. The carbonyl clusters with the formula $M_3(CO)_{12}$, where M = Ru, Os, Fe, have sufficient number of electrons to enable each metal atom to obey the inert gas rule, that is, to have 36 electrons around each atom. This situation is also expressed by saying that each metal atom has an 18-electron closed shell configuration. $Fe_3(CO)_{12}$ has structure IV which contains two bridging CO groups whereas $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ have structure V containing all carbonyl groups as terminal CO groups.



$Fe_3(CO)_{12}$

(IV)

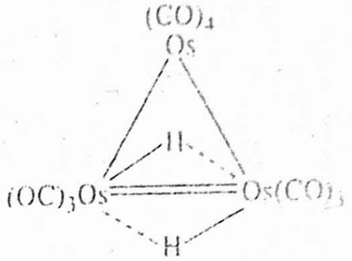


$M_3(CO)_{12}$ (M = Ru, Os)

(V)

The CO group in $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ can be replaced by CH_3CN. The mixed carbonyls, thus obtained, are quite reactive.

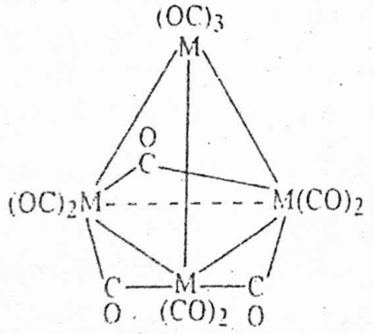
Generally, in polynuclear carbonyl clusters, the metal atoms are bonded through metal—metal single bonds. In the hydrido carbonyl cluster, $H_2Os_3(CO)_{10}$, however, the metal atoms are bonded with each other through a double bond, as shown in structure VI.



$H_2Os_3(CO)_{10}$

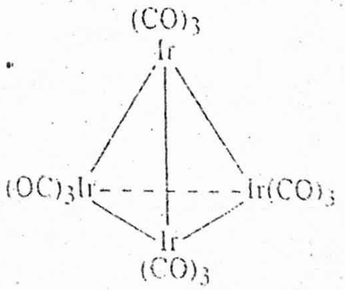
(VI)

Many homonuclear and heteronuclear **tetranuclear carbonyl clusters** containing four metal atoms are also known. Most of them display tetrahedral cluster structures. The structures of $M_4(CO)_{12}$ where M = Co, Rh, Ir, are shown below (Structures VII, VIII). In these carbonyls also, each metal atom has an 18–electron closed shell configuration.



$M_4(CO)_{12}$ (M = Co, Rh)

(VII)



$Ir_4(CO)_{12}$

(VIII)

Some tetranuclear carbonyl clusters also exhibit butterfly and planar cluster structures of the type shown (Structures IX and X).

Butterfly cluster structure

(IX)

Planar cluster structure

(X)

It may be noted that the procedure of electron counting in LNCC's is the same as used for electron counting in mononuclear carbonyls discussed in the last chapter.

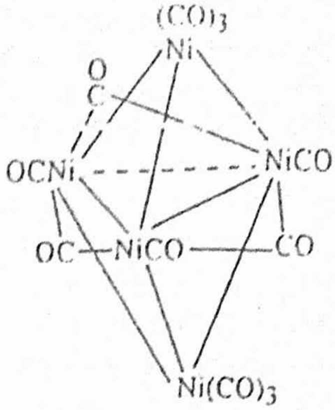
b. High Nuclearity Carbonyl Clusters (HNCC). These clusters contain five or more than five metal atoms directly bonded to one another. A large number of such carbonyl clusters have recently been isolated. Examples are $Rh_6(CO)_{16}$, $Ru_6(CO)_{18}H_2$ and $\{(Ni_3(CO)_6\}_n^{2-}$. Many mixed carbonyl clusters containing encapsulated carbon atom are also known. Many of these carbido carbonyl clusters can be prepared either by pyrolysis or by refluxing metal carbonyls for long periods in solvents such as $CHCl_3$

example, consider the carbonyl $Fe_3(CO)_{12}$. The total electron count in this case is 48 and the skeletal electron pairs available for framework bonding are 1/2(48—36)=6, *i.e.*, 3+3. The Fe_3 cluster in $Fe_3(CO)_{12}$ thus has an arachno structure derived from (3+2)-vertex polyhydron (*i.e.*, trigonal bipyramid) whose two axial vertices are removed leaving an effectively triangular geometry for the Fe_3 cluster in this carbonyl.

Similarly, the structure of $Co_4(CO)_{12}$ is rightly predicted by Wade's rules to have been derived from a (4+1)-vertex polyhydron (*i.e.*, trigonal bipyramid) whose one axial vertex is removed to give an effectively tetrahedral geometry for the Co_4 cluster in this carbonyl. It is worth remembering that a trinuclear LNCC generally has a total electron count of 48 and a tetranuclear LNCC generally has a total electron count of 60.

It will not be out of place to mention that although Wade's rules can predict the structures of a majority of polyhedral carbonyl clusters yet there are a few exceptions to these rules as well.

For example, the structure of $[Ni_5(CO)_{12}]^{2-}$ is predicted (by Wade's rules) to be arachno whereas actually it is found to be closo trigonal bipyramidal (Structure XIV).



$[Ni_5(CO)_{12}]^{2-}$
(XIV)

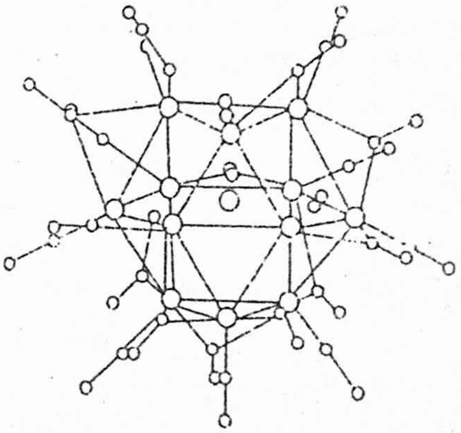
We have so far discussed carbonyl clusters of mostly Fe, Ru and Os. A few of the carbonyl clusters of Co, Rh and Ir will also be discussed briefly. Of the latter, Rh forms the largest number of carbonyl clusters followed by Co. The number of Ir carbonyl clusters is limited.

Rhodium carbonyl clusters consisting of 5 to 22 Rh atoms often adopt structures that have an interstitial Rh atom within a polyhedron of Rh atoms as in $[Rh_{13}(CO)_{24}H_2]^{3-}$ in which the arrangement of Rh atoms is a fragment of hexagonal closed packed array as shown (Structure XV).

Rh also forms mixed metal clusters, especially with Pt. An example is furnished by $[PtRh_8(CO)_{19}]^{2-}$.

Co forms high nuclearity carbonyl clusters with metal atoms ranging between 5-16.

Apart from the above, high nuclearity carbonyl clusters of some other metals are also known. Examples are carbonyl clusters of Ni, Pd and Pt.



$[Rh_{13}(CO)_{24}H_2]^{3-}$
(XV)

Nickel carbonyl clusters can be synthesised by reacting $Ni(CO)_4$ with an alkali metal in THF.

$$Ni(CO)_4 \xrightarrow[THF]{\text{Alkali metal}} [Ni_5(CO)_{12}]^{2-} + [Ni_6(CO)_{12}]^{2-}$$

$$[Ni_6(CO)_{12}]^{2-} \xrightarrow{FeCl_3} [Ni_9(CO)_{18}]^{2-}$$

The carbonyl cluster $[Ni_6(CO)_{12}]^{2-}$ when refluxed in CCl_4, gives a number of carbide carbonyl [illegible] $[Ni_8C(CO)_{16}]^{2-}$, $[Ni_9C(CO)_{17}]^{2-}$ and $[Ni_{10}C(CO)_{18}]^{2-}$.

A number of mixed carbonyl-trimethyl phosphine clusters of Pd are known. These have the formula [illegible] $(PMe_3)_7$ and $Pd_{10}(CO)_{18-n}(PMe_3)_n$ where *n* ranges from 1 to 17. Both these structures contain a Pd_6 octahedron which is capped by one and four Pd atoms, respectively.

The platinum carbonyl clusters, that have been discovered only recently, can be divided into the following two categories :

1. Columnar platinum clusters with the general formula $[(Pt_3(CO)_6]_n^{2-}$ (*n* varies from 2 to 5) whose

structures are built up by stacking planar $Pt_3(CO)_6$ units one above the other. The stacking is essentially prismatic.

2. Large platinum cluster anions such as $[Pt_{19}(CO)_{22}]^{4-}$, $[Pt_{38}(CO)_{44}]^{2-}$ and $[Pt_{26}(CO)_{32}H_n]^{2-}$ (the value of n is uncertain). The first cluster anion has D_{5h} symmetry and the last two have approximately cubic close packed array of Pt atoms and seem to have properties bordering between those of molecular and bulk metals.

Recently some mixed Ni–Pt clusters have also been synthesised.

2. HALIDE TYPE CLUSTERS

The best known dinuclear clusters of this type have the general formula $[Re_2X_8]^{2-}$ (X = Cl, Br, I, NCS, etc.). These clusters possess the following typical structural features :

a. They have short Re—Re distance of 2.24 Å compared with Re—Re distance of 2.75 Å in bulk metal.

b. They possess eclipsed conformation which seems to be rather surprising. Since the sum of the van der Waals radii of two Cl atoms is more than the experimentally observed distance between the two chlorine atoms attached to the two separate Re atoms, one would have expected a less sterically crowding staggered conformation to be more stable. Both the conformations are shown in Fig. 1.

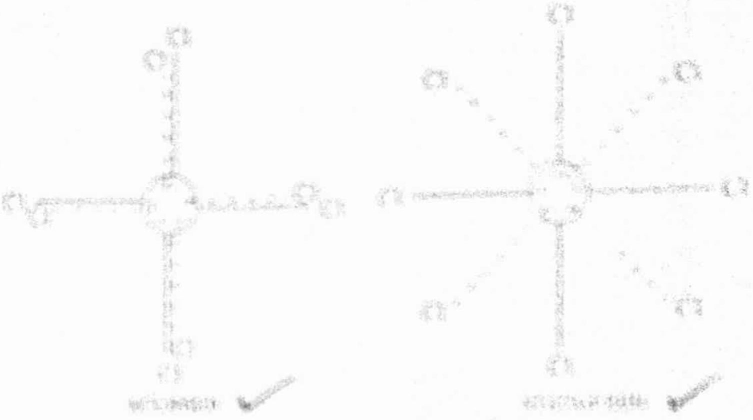


Fig. 1. Eclipsed and staggered conformations of $[Re_2X_8]^{2-}$

A plausible explanation for both the above mentioned observations is given below :

1. The $d_{x^2-y^2}$, s, p_x and p_y orbitals of each Re atom hybridise to give four dsp^2 hybrid orbitals on each Re atom. These hybrid orbitals accommodate 8 electrons donated by the four chloride ions attached to each Re.

2. The d_{z^2} and p_z orbitals of each Re atom hybridise to give two dp hybrid orbitals on each Re atom. A dp hybrid orbital of one Re atom overlaps with a similar orbital on the other Re atom to yield a σ (bonding) and a σ* (antibonding) molecular orbital. Each Re atom is thus left with a nonbonding dp hybrid orbital. This is diagrammatically shown in Fig. 2 (σ* orbital is not shown).

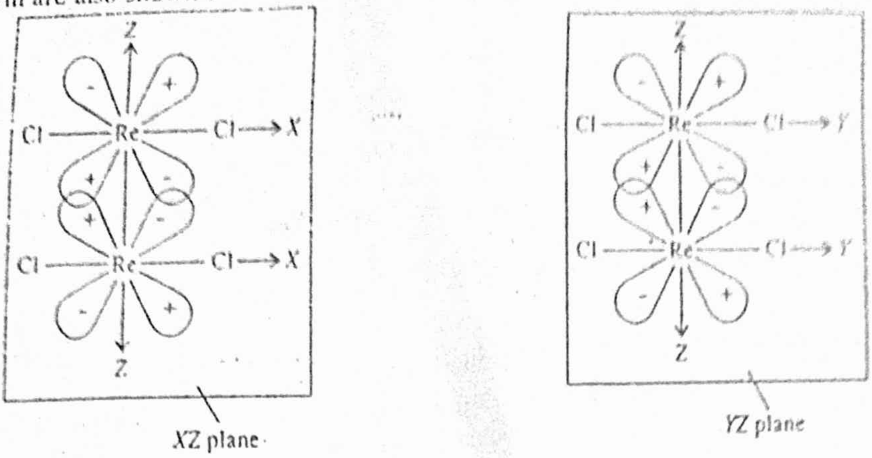
dp hybrid σ bonding molecular orbital

[illegible]

Fig. 2. σ bonding and nonbonding [illegible]

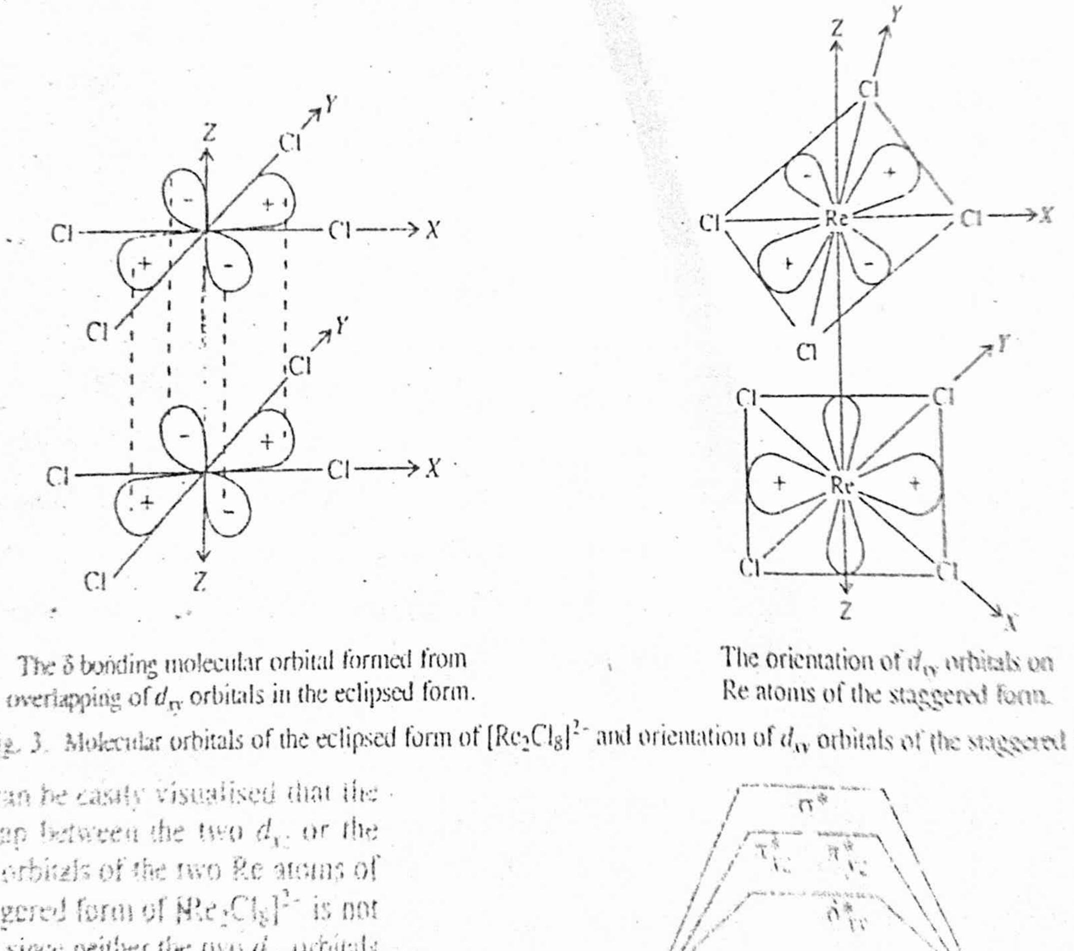
3. The d_{xz} orbitals of the two Re atoms of the eclipsed form, being in the same XZ plane, therefore, overlap with each other to give π_{xz} (bonding) and π_{xz}^* (antibonding) molecular orbitals.

Similarly, the d_{yz} orbitals of the two Re atoms of the eclipsed form, being in the same YZ plane, overlap with each other to give π_{yz} (bonding) and π_{yz}^* (antibonding) molecular orbitals. The d_{xy} orbitals of the two Re atoms of the eclipsed form are of proper symmetry to give sideways overlap yielding δ (bonding) and δ* (antibonding) molecular orbitals. The π and δ bonding molecular orbitals of the eclipsed form of $[Re_2Cl_8]^{2-}$ are shown in Fig. 3. The d_{xy} orbitals of the two Re atoms of the staggered form are also shown :



π_{xz} bonding molecular orbital of eclipsed form (The Cl atoms along Y-axis direction are not shown)

π_{yz} bonding molecular orbital of eclipsed form. (The Cl atoms along X-axis are not shown)



The δ bonding molecular orbital formed from overlapping of d_{xy} orbitals in the eclipsed form.

The orientation of d_{xy} orbitals on Re atoms of the staggered form.

Fig. 3. Molecular orbitals of the eclipsed form of $[Re_2Cl_8]^{2-}$ and orientation of d_{xy} orbitals of the staggered form.

It can be easily visualised that the π overlap between the two d_{xz} or the two d_{yz} orbitals of the two Re atoms of the staggered form of $[Re_2Cl_8]^{2-}$ is not possible since neither the two d_{xz} orbitals are in the same plane nor are the two d_{yz} orbitals so. Also, as is clear from the figure given above, the lobes of the two d_{xy} orbitals on Re atoms of the staggered form are not properly placed for a δ overlap.

The qualitatively drawn molecular orbital energy level diagram for Re—Re bonding in the eclipsed form

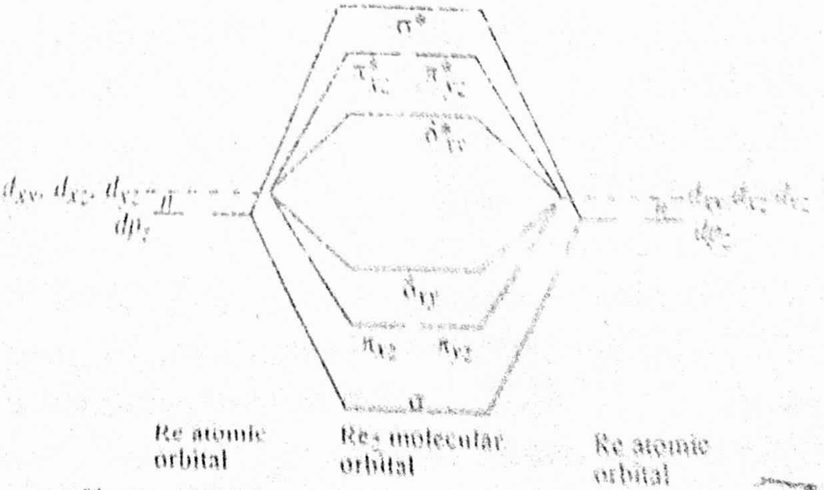


Fig. 4. Molecular orbital energy level diagram for Re—Re [illegible]

Complex

The oxidation state of Re in $[Re_2Cl_8]^{2-}$ is +3 and hence Re in this anion has d^4 configuration. The eight electrons of the two Re atoms would occupy one σ, two π and one δ bonding molecular orbitals. There is thus a quadruple bond between the two Re atoms. This explains both the observations (i) and (ii) mentioned above, i.e., the short Re—Re distance and the existence of eclipsed form only for $[Re_2Cl_8]^{2-}$.

There are a number of other dinuclear compounds which have eclipsed form and have short M—M distances due to the existence of multiple bonds between the metal atoms. Examples are the carboxylate complexes of the general formulae $Re_2(RCOO)_4X_2$ and $Mo_2(RCOO)_4$. The metal ions in these complexes have d^4 configuration. Their skeletal structures are shown in Fig. 5. (The lines between the atoms do not show the exact bond order).

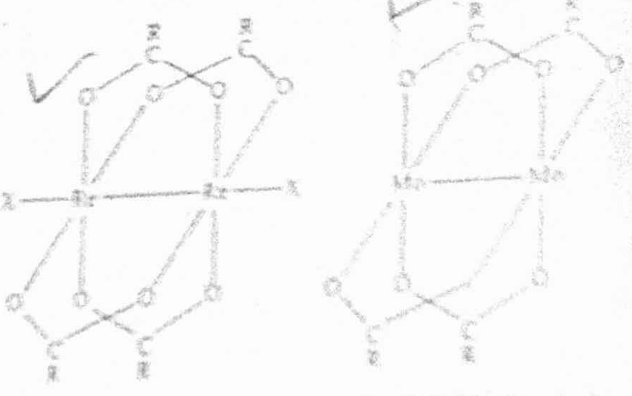


Fig. 5. The skeletal structures of $Re_2(RCOO)_4X_2$ and $Mo_2(RCOO)_4$

In both the above compounds the eight electrons from four oxygen atoms coordinated to each metal atom occupy $d_{x^2-y^2}sp^2$ hybrid orbitals of each metal atom. The two ligands X⁻ in $Re_2(RCOO)_4X_2$ donate two pairs of electrons to the two vacant nonbonding dp hybrid orbitals localised on each Re atom. Thus, the configuration of Re_2 in $Re_2(RCOO)_4X_2$ is $\sigma^2\pi^4\delta^2n^4$ and of Mo_2 in $Mo_2(RCOO)_4$ is $\sigma^2\pi^4\delta^2$. This results in a quadruple metal-metal bond in both the compounds leading to shortening of the metal-metal bonds compared to the metal-metal distances in the bulk metals.

The presence of quadruple bonds (specially π and δ bonds) in the above mentioned dinuclear complexes of Re and Mo favours the formation of the eclipsed form.

Calculations show that the energies of δ molecular orbital (bonding), dp hybrid orbital (non bonding) and δ* molecular orbital (antibonding) of the dinuclear metal clusters discussed above are very close to one another. Also the π and δ overlaps between the d orbitals of metals in these compounds lead to very weak bonds compared to bonds formed due to π overlap between p orbitals in the compounds of lighter metals.

Cupric carboxylates have also an eclipsed structure like the carboxylates of Re and Mo discussed above. However, the Cu—Cu distance in cupric carboxylate is longer than in the copper metal. This is probably due to the fact that the electron spins of the odd electrons of the two Cu^{2+} ions, each of which is a d^9 system, get mutually paired up leading to a single Cu—Cu bond. The structure of $Cu_2(RCOO)_4 \cdot 2H_2O$ is as shown (Structure XVI). It is difficult to explain the eclipsed conformation of the cupric carboxylates.

$M_2(RCOO)_4 \cdot 2H_2O$
(M = Cu, Cr)
(XVI)

The carboxylate $Cr_2(COO)_4 \cdot 2H_2O$ has a similar structure but the bond order of Cr—Cr bond is uncertain.

Another important class of dinuclear complexes are metal alkoxides of the formula $M_2(OR)_6$ (M = Mo, W).

The metal-metal multiple bonds in these compounds can be easily attacked as is obvious from the reaction given below:

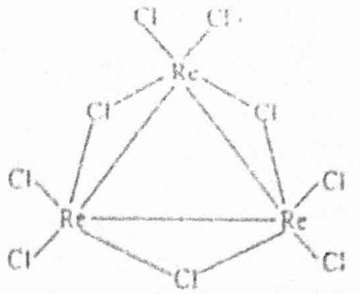
$$(RO)_3W{\equiv}W(OR)_3 + 2X_2 \longrightarrow X_2(RO)_3W—W(OR)_3X_2$$

(R = iPr, t Bu ; X_2 is halogen)

$W_4(OR)_{12}$

The compound $W_2(OiPr)_6$ can be dimerised. The dimer is a fluxional molecule in which double bonds and single bonds keep on exchanging places in the W_4 ring at room temperature. The alkoxy groups O-iPr also keep on exchanging places between the bridged and the terminal positions. The instant structure of $W_4(OR)_{12}$ is as shown [Structure XVII].

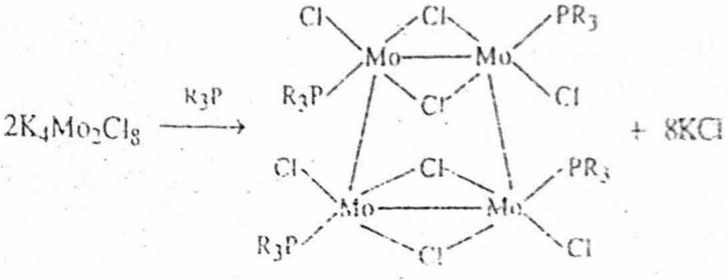
The trinuclear halide type clusters have the general formula Re_3X_9 (X = Cl, Br, I). The structure of Re_3Cl_9 is as shown (Structure XVIII). The lines do not show the exact bond order.



Re_3Cl_9
(XVIII)

Since the Re–Re distance in this trinuclear cluster is shorter than the distance in Re metal, the bond order between the Re atoms appears to be more than one. Of the two terminal chlorines on each Re atom, one is above and the other is below the triangular plane containing the three Re atoms. In the solid state, the trinuclear cluster retains the basic triangular structure but further bridging through chloro ligands occurs resulting in the formation of a polymeric structure. Re_3Cl_9 reacts with a number of ligands (L) to give $Re_3Cl_9L_3$. The solid Re_3Cl_9 dissolves in HCl to give $[Re_3Cl_{12}]^{3-}$. Both $Re_3Cl_9L_3$ and $[Re_3Cl_{12}]^{3-}$ have triangular structures.

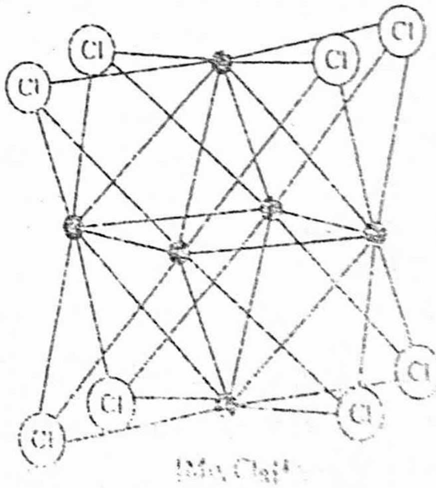
The tetranuclear halide type metal clusters are also known. We have already mentioned the dimerisation of dinuclear metal clusters containing metal-metal double bonds. For instance, the dinuclear alkoxide of $W_2(OR)_6$ dimerises to give a tetranuclear metal cluster $W_4(OR)_{12}$ whose structure has already been discussed above. The W=W bond in $W_4(OR)_{12}$ can be saturated to give $W_4(OR)_{16}$. Similarly, the dinuclear metal cluster $[Mo_2Cl_8]^{4-}$ containing Mo–Mo bond polymerises to give a tetranuclear metal cluster $Mo_4Cl_8(PR_3)_4$ (Structure XIX).



$Mo_4Cl_8(RP_3)_4$
(IX)

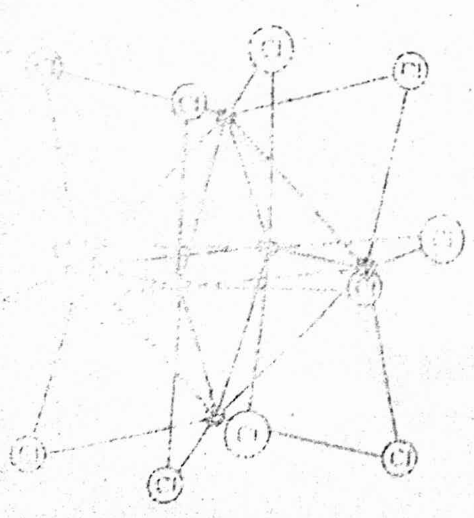
The lines in the above structure of the polymer do not show the exact bond order. Experimental evidence shows that there are alternate single and triple bonds in the Mo_4 ring in the above structure.

Mo, W and Ta form **hexanuclear metal clusters** of the type M_6X_8 and M_6X_{12}. In M_6X_8 type of clusters, each of the eight faces of M_6 octahedron is capped by a μ_3-X atom. A typical example is the metal cluster $[Mo_6Cl_8]^{4+}$ in which each Mo atom has d^4 configuration. The structure of $[Mo_6Cl_8]^{4+}$ is as shown (Structure XX).



$[Mo_6Cl_8]^{4+}$
Solid circles represent Mo atoms
(XX)

There are 12 Mo–Mo bonds in the Mo_6 octahedron and there are 6 × 4 = 24 valence electrons to form these 12 Mo—Mo bonds in $[Mo_6Cl_8]^{4+}$. Therefore, each Mo—Mo bond utilises one electron pair and is thus a normal single bond. Another hexanuclear metal cluster having similar structure is $[Mo_6S_8]^{4+}$. In the M_6X_{12} type of hexanuclear metal clusters, each of the 12 edges of M_6 octahedron is bridged by a μ_2-X atom. A typical example of this type is the cluster $[Nb_6Cl_{12}]^{2+}$ whose structure is as shown (Structure XXI).

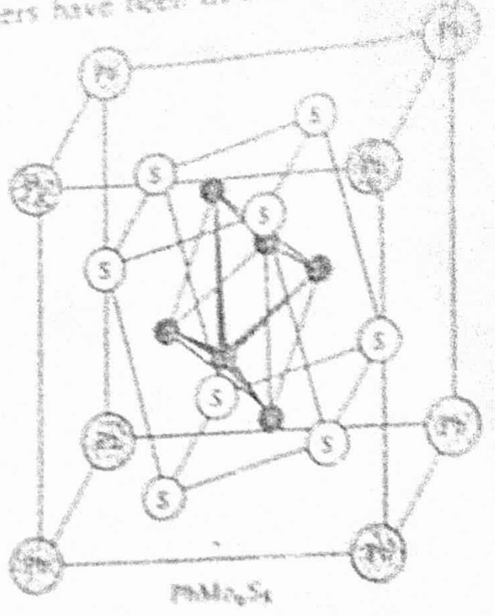


$[Nb_6Cl_{12}]^{2+}$
Solid circles represent Nb atoms
(XXI)

There are 16 valence electrons (i.e., 6×5 − 12 − 2) with Nb_6 octahedron which are used up to form 12 Nb—Nb bonds in Nb_6 octahedron. Thus, there are only 8 valence electron pairs for 12 Nb—Nb bonds of the metal cluster. Therefore, each Nb—Nb bond has a bond order of 8/12 or 2/3.

Some newly discovered metal clusters. Apart from the above two main categories of metal clusters (*i.e.*, carbonyl type and halide type), two new types of metal clusters have been discovered recently. These are named as *Chevrel phases* and *'Naked' Clusters* (or clusters without ligands). The 'naked' clusters are also called *Zintl ions*. A brief description of these newly discovered clusters is given below.

✓1. **Chevrel Phases.** These are mixed Mo clusters having the general formula $M_xMo_6X_8$ where M represents a metal such as Pb, Sn, Cu, Co and Fe and X represents S, Se and Te. These clusters are named after their discoverer Roger Chevrel. The arrangement of atoms in one such compounds, namely, $PbMo_6S_8$ is as shown (Structure XXII).



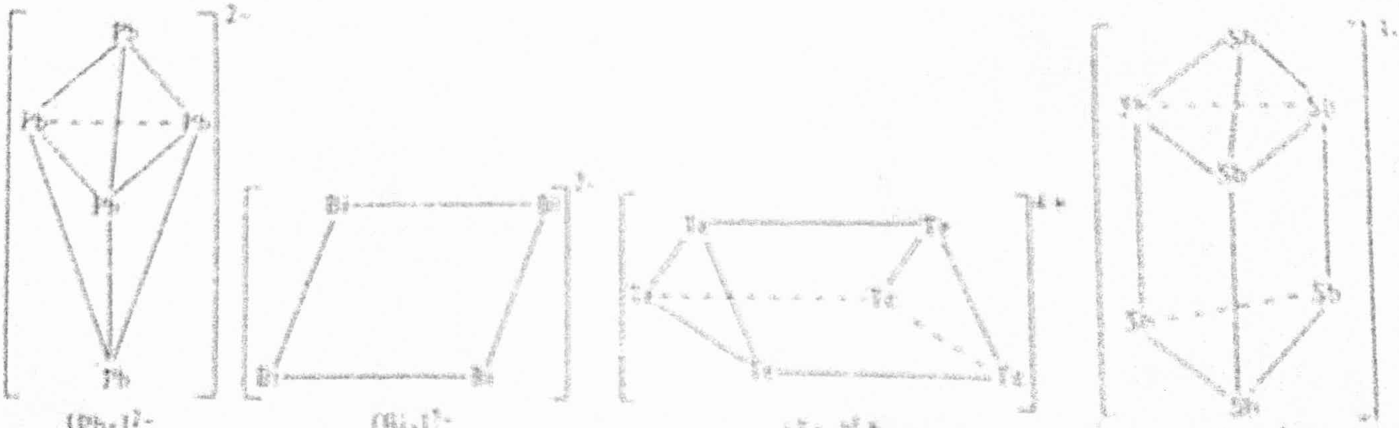
$PbMo_6S_8$

Solid circles represent Mo atoms

(XXII)

The structure may be considered as an octahedral cluster of Mo atoms surrounded by a cubic cluster of eight S atoms which, in turn, is surrounded by a cubic lattice of Pb atoms. The Chevrel compound $PbMo_6S_8$ is a super conductor below 13·3° K.

✓2. **Zintl Ions or 'Naked' Clusters or Clusters Without Ligands.** Some post transition metal alloys with sodium (known as Zintl alloys) dissolve in liquid ammonia to give highly coloured ions such as Sn_9^{4-}, Sb_7^{3-}, Bi_4^{2-}, Pb_5^{2-}, Bi_9^{5+}, Te_6^{4+}, etc. Such polyatomic ions are referred to as **Zintl ions** or **'naked' clusters**. The cluster structures of some of the Zintl ions are shown in Fig. 6.



$[Pb_5]^{2-}$ $[Bi_4]^{2-}$ $[Te_6]^{4+}$ $[Sb_7]^{3-}$

Fig. 6. Cluster structures of some Zintl ions.

QUESTIONS

1. What is a metal cluster ? Illustrate giving suitable examples.
2. What are [illegible] and [illegible] and bonding in low nuclearity and high nuclearity [illegible] clusters.
3. Describe the procedure for predicting the skeletal structure of [illegible] clusters. Are there any exceptions to the Wade's rules [illegible]
4. Discuss the structures of the following [illegible]
5. Discuss the structures of [illegible], [illegible], [illegible]
6. Discuss, on the basis of molecular orbital theory, the structure of $[Re_2Cl_8]^{2-}$
7. Taking suitable examples, discuss the structures of trinuclear, tetranuclear and hexanuclear halide type of metal clusters.
8. Discuss the structures of [illegible] and its dimer.
9. Discuss the structure and bonding in $[Nb_6Cl_{12}]^{2+}$
10. What are Chevrel phases and Zintl ions ? Discuss the [illegible]