Subject	Chemistry
Paper No and Title	11: Inorganic Chemistry-III (Metal π–Complexes and Metal Clusters)
Module No and Title	29: Metal-metal bonds and their evidences
Module Tag	CHE_P11_M29

Principal Investigator		Co- Principal Investigator and Technical Coordinator
Prof A.K.Bakhshi Sir Shankar Lal Professor, Department of Chemistry University of Delhi		**Dr Vimal Rarh** Deputy Director, Centre for e-Learning and Assistant Professor, Department of Chemistry, SGTB Khalsa College, University of Delhi *Specialised in : e-Learning and Educational Technologies*
Paper Coordinator	**Content Writer**	**Reviewer**
Prof. Ranjit K. Verma Professor Department Of chemistry Magadh University, Bodh Gaya, Bihar	**Dr. M. Sathiyendiran** Asst Professor Department of chemistry University of Delhi **Dr. Deepak Gupta** Assistant Professor Kirori mal college University of Delhi	**Prof. B.S. Garg** Emeritus Professor Department of Chemistry University of Delhi
Anchor Institute : SGTB Khalsa College, University of Delhi		

TABLE OF CONTENTS

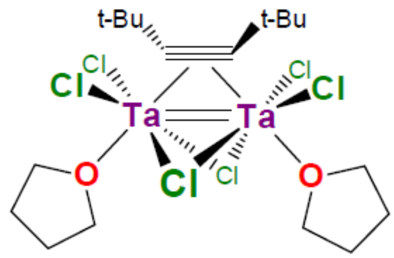
1. Learning Outcomes

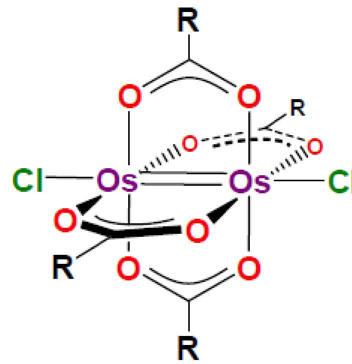
After studying this module, you shall be able to

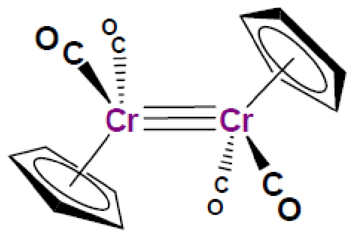
- Know about metal –metal bonds
- Learn types of metal-metal bonds
- Study examples of metal complexes having metal-metal single or multiple bonds
- Analyze spectroscopic evidences for the presence of metal-metal bond.

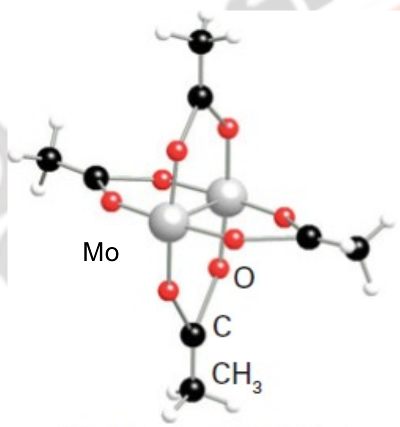
2. Introduction

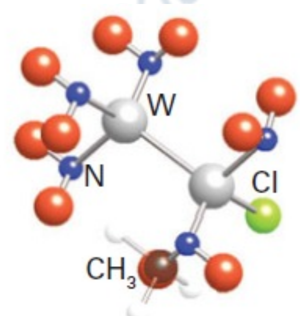
Metal-metal bond is a bond between two metal centers, particularly between two transition metal atoms, which ranges from a single to a quadruple bond. The existence of metal-metal bond is mainly because of the presence of (n+1)*s*, (n+1)*p* and n*d* orbitals as valence shell electronic configuration. The transition metals can form three general types of bonds such as covalent bonds, dative bonds and weak metal-metal symmetry interactions where covalent bonds being the strongest and symmetry interactions are the weakest. The compounds containing a large number of metal-metal bonds forming triangular and larger structures are called cluster compounds, however these also include linear M-M bonds. The metal clusters can also be defined as any entity that contains a metal-metal bond. The journey started with the identification of the Hg-Hg in the Hg_2^{2+} ion (Hg_2Cl_2) which was the first d-block metal-metal bonded species. Most of these cluster compounds are homo-metallic, however there are few exceptions with hetero-metallic cluster complexes .Some examples of clusters are shown below for reference:

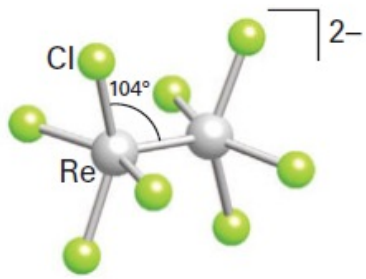

t-Bu
t-Bu
Cl
Cl
Ta
Ta
Cl
Cl
Cl
Cl
O
O


R
O
O
R
O
O
Cl
Os
Os
Cl
O
O
R
O
O
R


OC
OC
Cr
Cr
CO
CO


Mo
O
C
CH3


W
N
Cl
CH3


2–
Cl
104°
Re

3. Classification of metal clusters

Metal cluster have been classified in to two major catagories:

- The polynuclear carbonyl, nitrosyl and related clusters can be catagorized as Class I. These clusters are mainy formed by metals in lower oxidation states (-1, +1) which include the metal ions residing on the right hand side of the periodic table.

- The other category (Class II) includes clusters formed as halides and oxides of transition metal complexes in their higher oxidation states. The transition metals lying on the left hand side of the periodic table (second or third row transition metals) form such type of cluster compounds. For example, the $[Re_2Cl_8]^{2-}$ cluster contains a Re-Re single bond with +3 oxidation state on each rhenium center in the cluster.

Criteria for meal cluster formation:

- There is general trend that transition metals having large energies of atomization (Zr, Nb, Mo, Tc, Ru, Rh, Hf, Ta, W, Re, Os, Ir and Pt) display higher tendancy to form metal clusters.

- Nature of the *d*-orbital: The effective nuclear charge is inversely related to the size of the *d*-orbital. Higher nuclear charge tends to reduce the effective overlap of the *d*-orbitals which is unfavourable for cluster formation. For example, the first row transition metals with higher oxidation states (+2, +3) do not offer sufficient orbital overlap and therefore poses an unfavourable situation towards cluster formation.

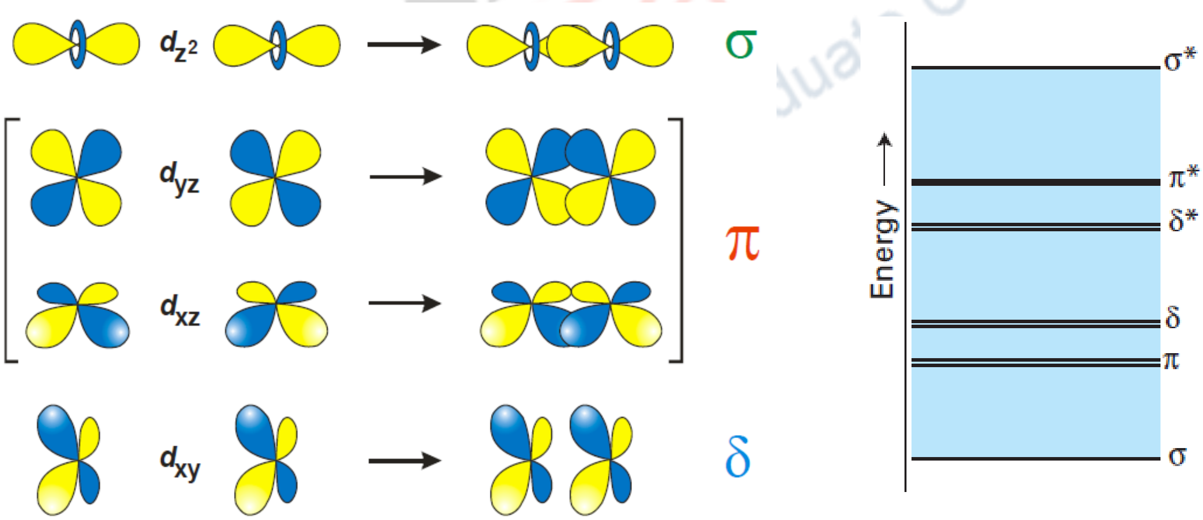
4. Metal-Metal bonding in metal clusters

There are three major types of bondings in metal cluster:

4.1 Covalent Bonding

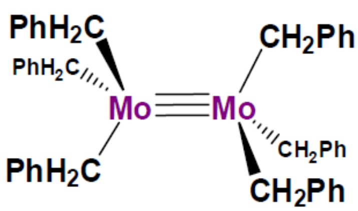
One electron from each metal atom constitutes a single M-M bond between the two metal atoms. This is the most common type of metal-metal bond ranging from a single to a quadruple metal-metal bond. Molecular orbital theory can be used to explain the overlap of various orbital to form three types of bonds namely the σ-bond, π-bond and the recently introduced δ-bond or the quadruple bond. Considering the possible overlap between the d-orbitals on adjacent metal atoms, one can figure out that:

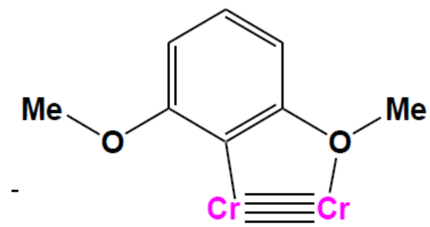
- A σ-bond between two metal atoms is a result of overlap of d_{z^2} orbital from each atom.
- Two π-bonds can be formed by the overlap of the d_{zx} and d_{yz} orbitals.
- Two δ-bonds can arise from the two face-to-face overlap of d_{xy} and $d_{x^2-y^2}$ orbitals. The $d_{x^2-y^2}$ orbital is also utilized for bonding with ligands.
-

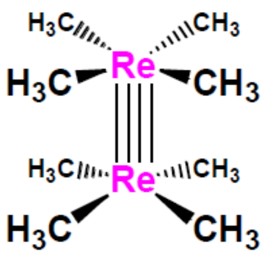


The energy diagram shown here points towards the possibility of a quintuple bond which could result when all the bonding orbitals are occupied to give an electronic configuration of $\sigma^2\pi^4\delta^4$.

Examples of multiple bonds containing metal clusters:

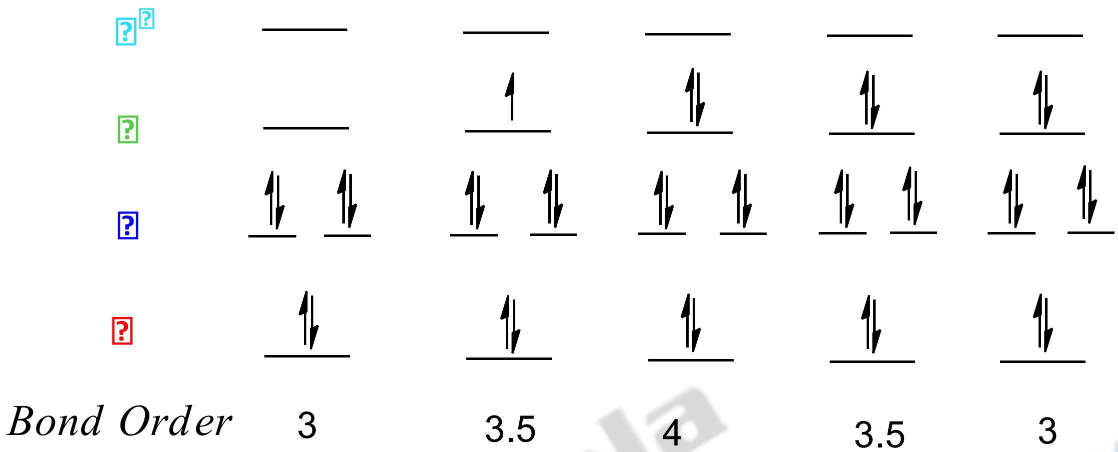






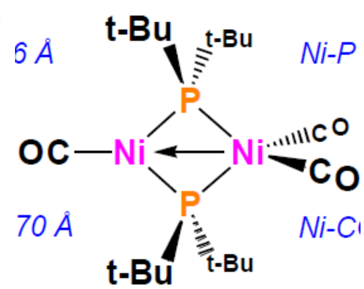
The table shown below is based on the criteria for cluster formation. As the number of electrons increases, the possibility of the formation of higher number of bonds between the two metal atoms increases. If the number of d-electron invlovled goe beyond eight, the electrons go to the anti-bonding orbitals and hence the number of bonds tend to decrease. In a case where the metal atoms having d^8 or d^{10} electronic configurations are involved, there is practically no chance of bond formation between the two metal atom due to the filling of anti-bonding orbitals.

Electron Count	Resulting M-M Bond
d^1 - d^1	Single bond
d^2 - d^2	Double bond
d^3 - d^3	Triple bond
d^4 - d^4	Quadruple bond ⟶ *optimum*
d^5 - d^5	Triple bond
d^6 - d^6	Double bond *(M-L bonding usually dominates)*
d^7 - d^7	Single bond
d^8 - d^8	No bond *(symmetry interaction)*



4.2 Dative Bond:

This type of bond is formed when one metal having filled d-orbitals coordinate to a metal atom containing empty d-orbitals by the donation of a lone pair of electron. Dative bonds are represented by an arrow instead of a line, starting from the donor metal and pointing to the undaturated metal atom. The bimetallic Ni complex has one dative bond.



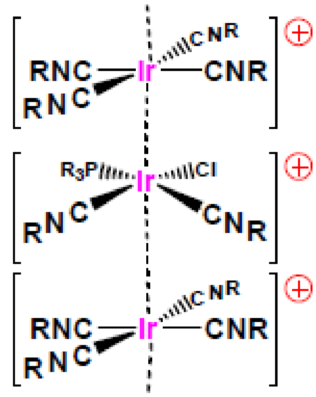
Ni-Ni = 2.41 Å

The donor Ni has a d^{10} electronic configuration whereas the acceptor nickel atom has a d^{8} (Ni(II)) electronic configuration.

4.3 Weak metal-metal symmetry interactions:

The weak metal-metal symmetry interactions are a result of symmetrical overlap of molecular orbital. This overlap is generally between filled and empty metal-metal bonding and/or anti-bonding orbitals. These interactions are typically seen in few bi- or polymetallic d^8 complexes both in solution and in the solid state.

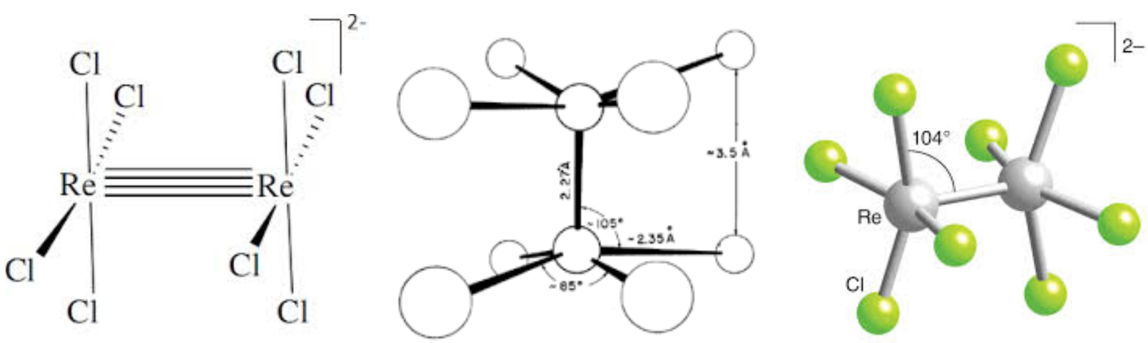
For example, the Ir tetrakis(isocyanide) complexes form oligomeric chains through M-M interacted stacks in solution and in the solid state without showing any evidence of a metal-metal covalent bond. These interactions were initially studied by Harry Gray who proposed that these interactions are caused by a molecular orbital symmetry interaction between the filled orbitals and empty anti-bonding molecular orbitals.

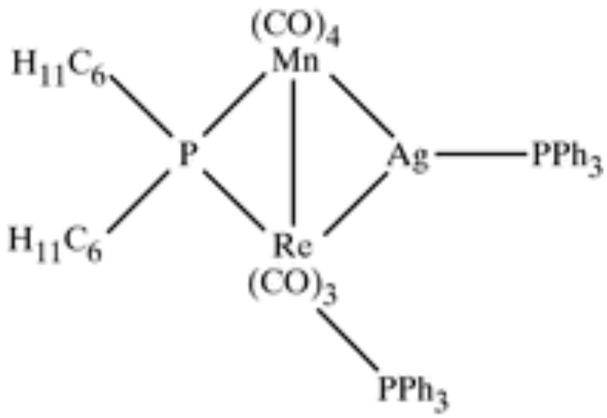


5. Types of metal-metal clusters

5.1 Dinuclear clusters:

The first dinuclear culster studied in detail was the species $[Re_2X_8]^{2-}$. The structural features were studied by Prof. F. A. Cotton. Surprisingly, the Re-Re bond distance was found to be 224 pm which is very less than the average Re-Re distance 275 pm in Re metal. Secondly, the distance between the chlorine atoms is nearly 330 pm which is less than the sum of their van der Waals radii (340-360 pm)

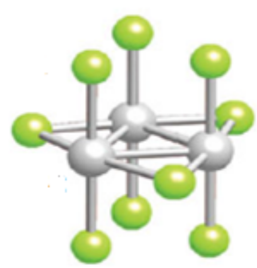




Cotton introduced the concept of a quadruple bond between the two rhenium centers. The chlorine atoms are connected to the rhenium ion in a square planar array. These are arranged in a staggered configuration forming a square anti-prism rather than a cube. Few other examples which involves metal-metal multiple bonded cluster are the hexa-alkoxo dinuclear tungsten and molybdenum complexes of the formula $[M_2(OR)_6]$ where M = Mo, W.

5.2 Trinuclear cluster:

Among all, the best studied examples of trinuclear clusters are those of Re such as rhenium trihalides $[(ReCl_3)_3]$ and their derivatives.

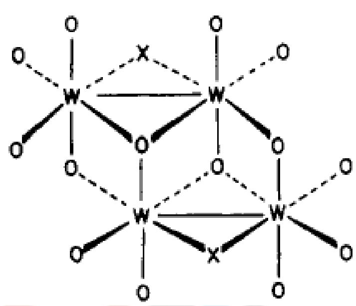


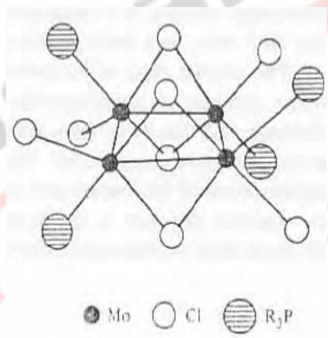
Re_3Cl_9

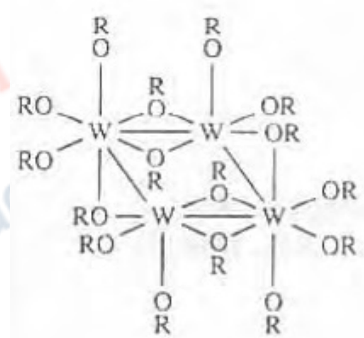
Each rhenium atom is bonded with the other two rhenium atoms by a metal-metal single bond. They are also bonded indirectly to three bridging chloride atom whereas each rhenium ion is also bonded with two chloride ions above and below Re triangular planes. The rhenium atoms form a triangle. The Re(III) ions have a d^4 configuration. If Re ions are bonded with Re-Re single bonds only, the complex would have been a paramagnetic complex. However, the complex is diamagnetic which implies that the Re ions are doubly bonded.

5.3 Tetranuclear cluster:

A number of tetranuclear cluster are known in the literature where most of them exist as halides and oxides of tungsten and molybdenum, metals.



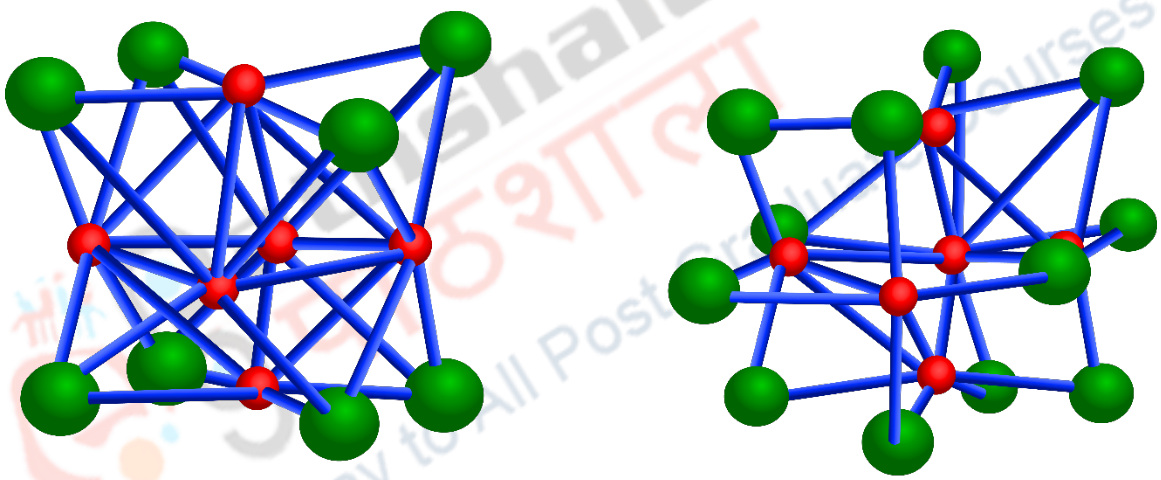




5.4 Hexanuclear Cluster:

Metal clusters containing six metal atoms have been known for many years; mostly consist of molybdenum, niobium and tantalum atoms. Considering the case of metal chlorides, the first type of hexanuclear cluster consist of an octahedron of six metal atoms surrounded by eight chloride ions one on each face of the octahedron. In this way, the chloride ions are forming a cube around the metal octahedron. For example, such kind of arrangement can be seen in 'molybdenum dichloride' Mo_6Cl_{12} which can also be formulated as $[Mo_6Cl_8]Cl_4$. In this case, each Mo(II) ion is sharing four single bonds with four other Mo(II) ions and also receive four dative bonds from four chloride ions.

In the second type, twelve halide ions are surrounding the Mo octahedron and placed along the edges. Such types of clusters are formed by niobium and tantalum. Unlike the bonding situation in hexanuclear metal clusters discussed above, each metal ion is surrounded by a distorted square prism of four metals and four chloride ions. These compounds are electron deficient.



(a) (b)

Structure of (a) $Mo_6Cl_8^{2-}$ (b) $M_6X_{12}^{2+}$ (M (red balls) = Nb, Ta; X(Green balls)Cl, Br)

6. Summary

- Multi-metallic metal complexes possessing metal-metal bonds are called cluster compounds. They are of variety of geometries such as linear metal-metal bonds, triangular and larger. There can be homo-metallic as well as hetero-metallic metal-metal bonds.

- The metal cluster can be classified on the basis of oxidation state of the metal ion and the bonded ligands. For example, the metal clusters containing halides or oxides as ligands are generally formed by metals in higher oxidation states.

- Metals cluster display mainly three types of bonds namely, covalent bonds, dative bonds and weak metal-metal symmetry interactions. Among these, covalent bond is the most prevalent one.

- Metal clusters display single to quintuple metal-metal bonds where molecular orbital diagrams can be used to explain the properties of a particular type of bond.

- The various types of metal clusters are dinuclear, trinuclear, tetranuclear and hexanuclear clusters.