

METAL CLUSTERS

A.ANTO AROCKIA RAJ

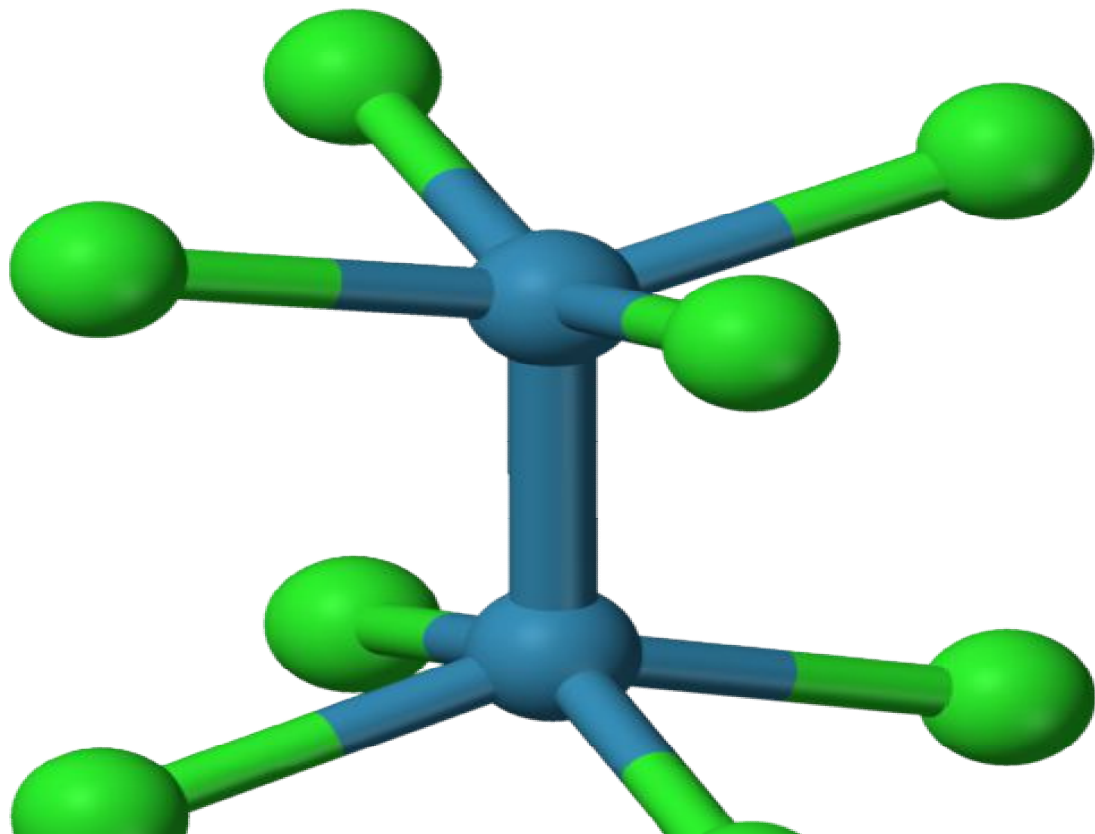
Assistant Professor

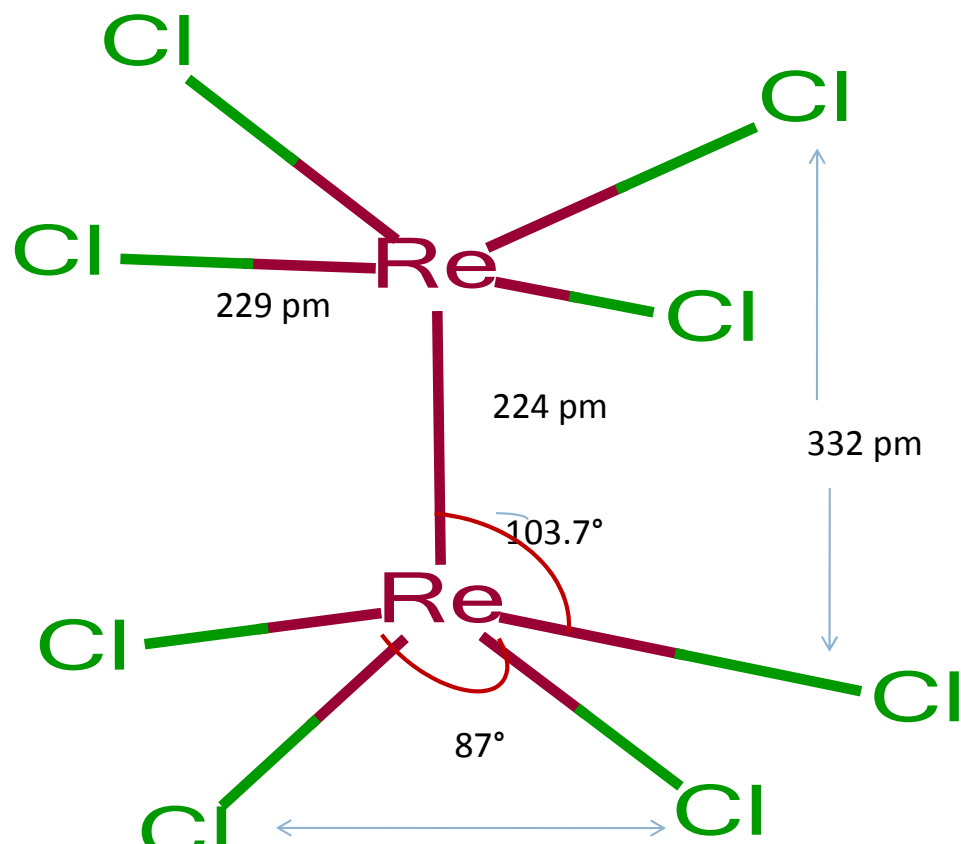
Dept. of chemistry

St. Xavier's College (Autonomous)

Palayamkottai

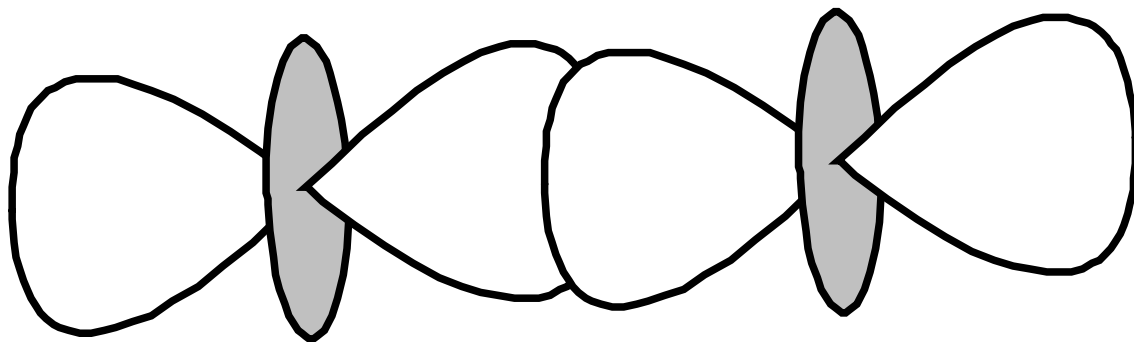
- The phrase *cluster* was coined by F. A. Cotton in 1960
- Refer to compounds containing metal–metal bonds
- The eclipsed structure of Potassium octachlorodirhenate(III) $\text{K}_2\text{Re}_2\text{Cl}_8$ was explained by invoking Quadruple bonding.
- A **quadruple bond** is a type of chemical bond between two atoms involving eight electrons.
- Quadruple bonds are most common among the transition metals in the middle of the d-block, such as Re, W, Mo and Cr.
- The quadruple bond was first characterized in



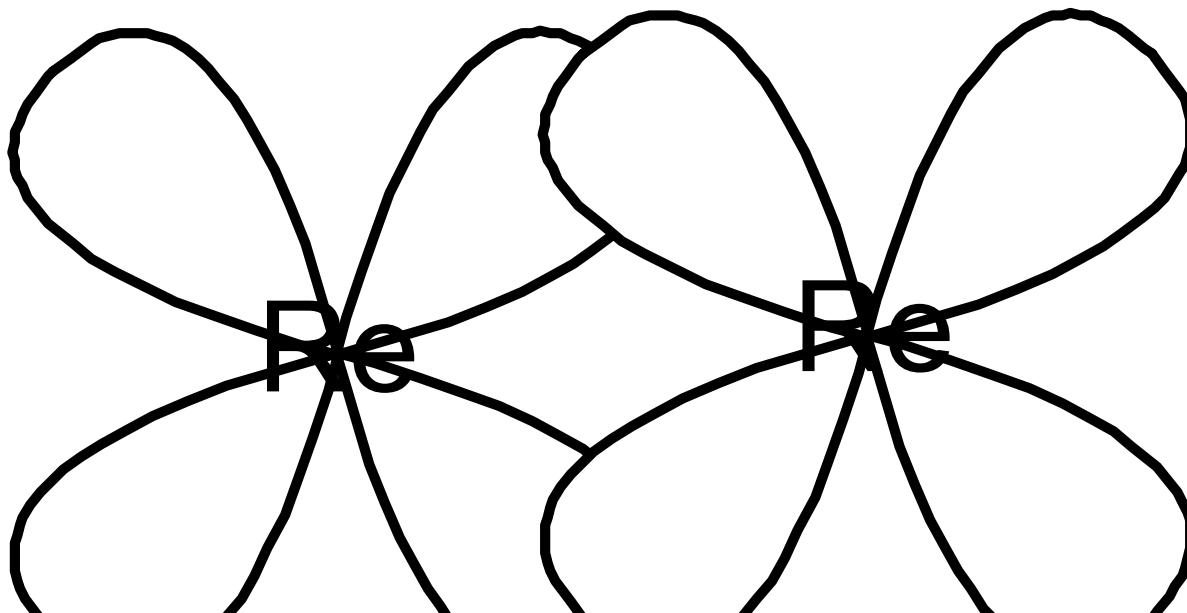


- Short Re – Re distance of 224pm.
- Chlorine atoms are placed in eclipsed manner
- Each Re experiences approximately a Square planar geometry with 4 Cl atoms and having the hybridisation dsp^2
- The d orbital involved here is $d_{x^2-y^2}$ orbital.
- The metal d_z^2 and p_z orbitals lie along the bond axis.
- The d_z^2 orbital of the two Re atoms overlap to form a

Formation of a σ bond from overlap
of d_z^2 orbital of each Re atoms



Formation of a Π bond from overlap of the d_{xz} orbital of each Re atom

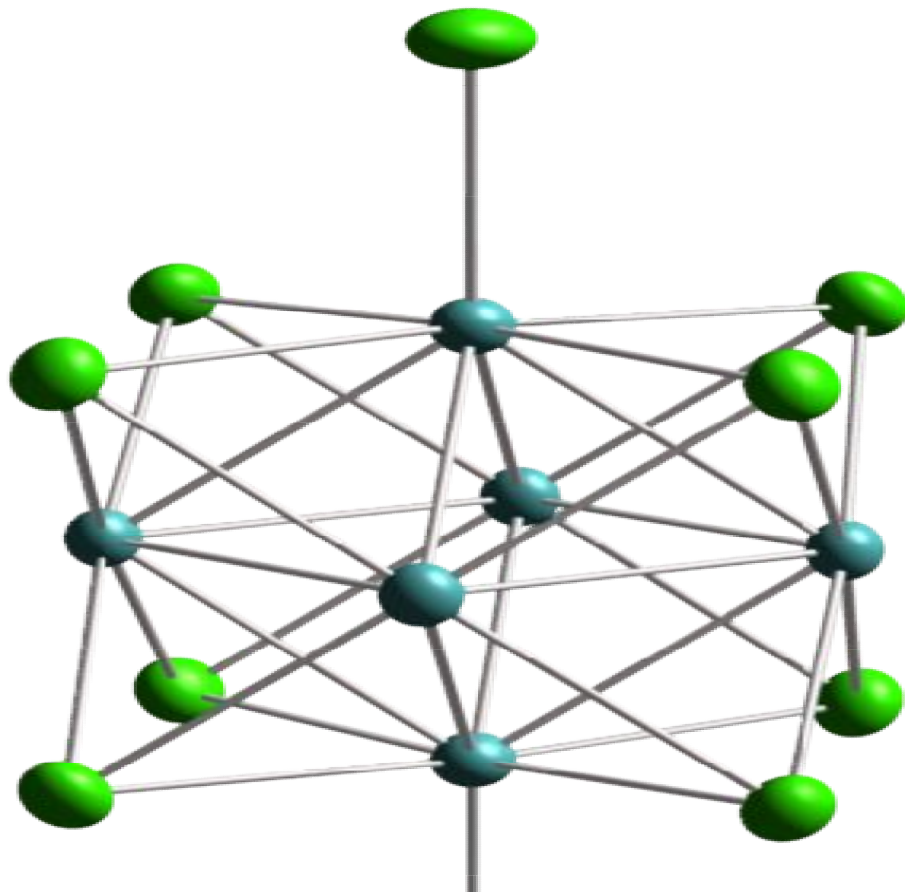


- The d_{xz} and d_{yz} orbitals of each Re overlap obliquely to form Pi bond (Π - bond).
- The d_{xy} orbitals of both Re atoms overlap sideways to form a delta bond (δ - bond)
- Overlap of d_{xy} orbitals can only occur if the chlorine atoms are eclipsed conformation. If the Cl atoms are staggered results zero overlap.
- The bonding is described as $\sigma^2\pi^4\delta^2$ with one sigma bond, two pi bonds and one delta bond

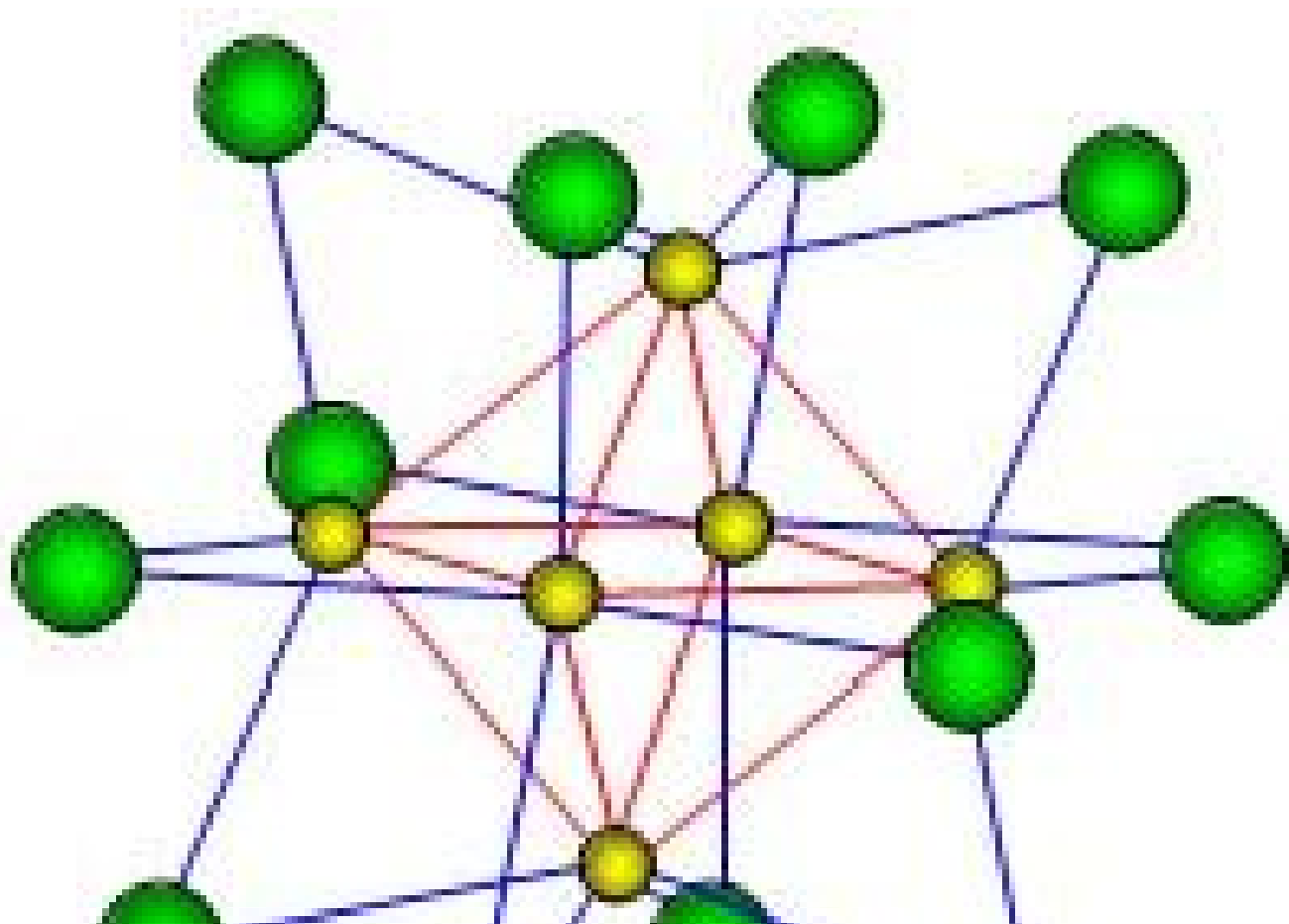
- The Re^{3+} (d^4) ion with Cl^- forms a dative bond
- The eight d-electrons from the two metals involved in quadruple bonding, hence the complex is **diamagnetic**.

Hexanuclear Clusters

- Hexanuclear Clusters- Mo, W, Nb and Ta.
- Two types of Hexanuclear Clusters
- An octahedron of six metal atom is coordinated by eight chloride ligands, one on each face of the octahedron this is formulated as $[\text{Mo}_6\text{Cl}_8]^{4+}$
- Each Mo(II)atom use its four electron to form four bonds with adjacent Mo atoms and receive dative bond from the four Chloride ligands.



- An octahedron of six metal atom is coordinated by twelve chloride ligands, one on each edges of the octahedron.
- Nb and Ta form clusters of this type and formulated as $[\text{Nb}_6 \text{Cl}_{12}]^{2+}$
- The metal atoms are surrounded by a very distorted square prism of four metal and four halogen atoms.
- These compounds are electron deficient like boranes.



THANK YOU