Synthesis of Chalcogenide Metal Cluster containing Phosphine ligands

A Dissertation

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By

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CERTIFICATE

This is to certify that the dissertation entitled “**Synthesis of Chalcogenide metal clusters containing phosphine ligands**” being Submitted by ***Puspanjali Bal*** to the Department of Chemistry, National Institute of Technology, Rourkela, Orissa, for the award of the degree of Master of Science is a record of bonafide research carried out by her**.** Under my supervision and guidance. To the best of my knowledge, the matter embodied in the dissertation has not been submitted to any other University / Institute for the award of any Degree or Diploma.

N.I.T. Rourkela**.**

Date: ***Dr. Saurav Chatterjee***

(Supervisor)

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Rourkela

Date: (Puspanjali Bal)

1.1 Clusters

Clusters are aggregates of atoms and molecules intermediate in size between the bulk matter and the individual atoms and molecules. They can be classified as small, medium-sized and large depending upon the number of constituent atoms or molecules, (a) Clusters can be homogeneous that is made of one kind of atom or molecule, (b) Heterogeneous- made of more than one kind of atoms. Clusters may be composed of any number of atoms or molecules. The most 'stable' cluster depends upon the number of particles into it.

1.2 Properties of Clusters

Cluster science is one of the most active and evolving fields of research in chemistry. These cluster system bridge the domains of atomic and molecular physics on one part and condensed matter physics on the other. Cluster show discrete spectroscopy due to their finite size [1]. Some of the points are illustrated which determines the importance of cluster in present day:

1. Cluster properties are influenced by electron delocalization. Quantum mechanical degrees of freedom help to give rise to shell structure and magic numbers in cluster. In metal and semi-conductor cluster, the electronic shell structure and geometric shell structure determines the shape and stability.
2. The existence of spherical shells in a metal clusters, phase change into amorphous of clusters and their thermal stability determines the cluster geometry.
3. The magnetic behavior differs in the size regime from bulk behavior. The enhancement in magnetic moment is due to strong d-electron localization.
4. Interaction of cluster with external fields like strong lower fields has to be evaluated which is quite important now a days.

   Metal cluster have several properties that suggest they are useful catalysts. The absence of large bulk phases leads to high surface to volume ratio, which is advantageous in catalysts applications as this maximizes the reaction rate per unit amount of catalyst material, and minimizes the cost [2]. Metal cluster are characterized by high degree of fluxionality of surface ligand and adsorbates associated with low energy barrier to rearrangement of the species on the surface [3-4].

1.3 Transition metal clusters

A transition metal cluster is defined as a group of two or more metal atoms held together by direct or substantial metal-metal bonding. It is an ensemble bound intermediate in size between a molecule and a bulk solid. It exists in diverse stoichiometries and nuclearities. For example. Transition metals and main group elements form especially robust cluster. There are ligand which stabilizes clusters which include CO, phosphine, halides, isocyanides, alkenes and hydrides. These clusters are of interest because of their structural diversity and potential applications in field of catalysis. The transition metal clusters are important because of their role in bridging gap between homogeneous and heterogeneous catalysis, showing high optical activity and selectivity of the homogeneous catalyst. Di- and Poly-nuclear cluster are useful precursor for preparation of novel catalysis. [5] Some clusters are known for their presence in enzymes like nitrogenase and their activity in bio-catalysis.

The metal complexes with low nuclearity and uncoordinated pair of electrons are used as coupling agents for preparation of metal cluster [6]. Main group elements like P, As, S, Se etc. are used. The lone pair of electrons serves as initial point of contact of the incoming metal unit to cluster through the formation of donor- acceptor bond by using empty metal orbital formed by loss of ligand. The bridging ligand also influences the ligand elimination leading to a new metal-metal bond formation.

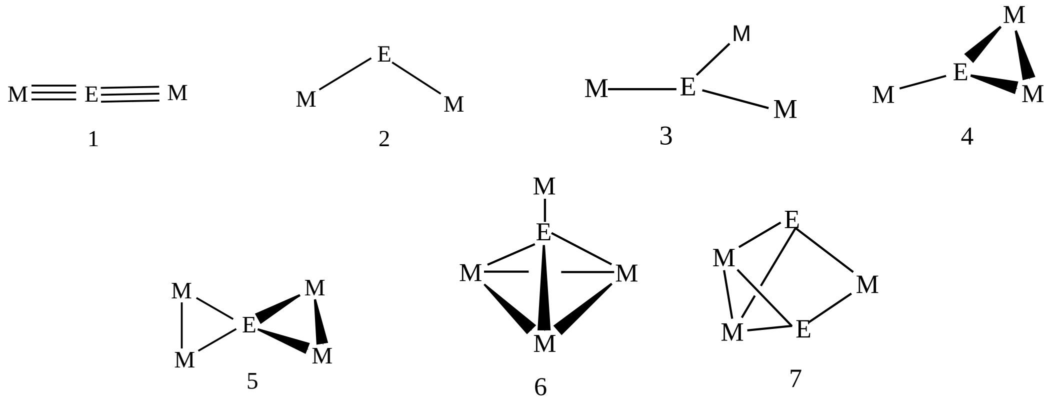
$$M_xE: + M_y' \rightarrow M_x(\mu\text{-}E) + My'$$

Some metal cluster also contains π-donor ligand, so they are considered as π-donor cluster or high oxidation state cluster as metal are in the high formal oxidation state. Group-7 to 10 metals has π-acceptor ligand like CO, PPh_3 ligand and is known as π-acceptor clusters or low oxidation state clusters. Metal ligand and metal-metal bond with π-acceptor ligand are kinetically inert towards bond dissociation or the fragmentation or colloid formation would take preference over clustering.

1.4 Transition metal cluster containing main group elements:-

Clusters are regarded as models of intermediate in catalysis and are itself used as catalysts. Many transition metal clusters are unstable which undergoes degradation so used for studies in organic transformation and catalysis. Main group bridging elements are important in clusters due to their effect of maintaining the integrity of the clusters which are required for catalysis. The main group elements are often added as promoters to give higher yields and better selectivity in many commercial catalytic reactions and also act as sites for reactivity. The formation of metal-metal bond is related to the steric bulk of the central main group element. The smaller main group element shows a greater tendency to support metal-metal bonding while heavier homologues generally bridge more open structures. The number of electrons contributed to the clusters by main group fragments depends on the presence of substituent on main group elements and the mode of binding.

Bridging ligand has been used as a means to promote the formation and stabilization of transition metal cluster complexes [7-10]. The incorporation of main-group elements into transition-metal carbonyl clusters introduces novel structural and reactivity features. Single-atom, main-group-element ligand are being increasingly used as bridges between different metal fragments in cluster growth reactions. These clusters often have the ability to add or remove ligand or electrons while retaining the cluster integrity.



E= Group. 13-16 elements, M= Transition metals).

Fig. 1. Structural geometries of transition metal cluster with main group elements.

1.5 Chalcogenide metal clusters:-

Clusters with unique structural features and unusual reactivities have been obtained by using chalcogen atoms as bridging ligand [11]. Chalcogen ligand display a wide variety of bonding modes when these are incorporated in transition metal carbonyl cluster frameworks. Chalcogen elements and transition-metal combine together to form discrete molecular structures which are of great interest due to their geometries and form new coordination and these are helpful as precursors for synthesis of new materials [12-14].

One of the advantages of using chalcogen in metal cluster is that when these ligand bridges with metals they prevent degradative fragmentation, to which clusters are usually susceptible during catalytic processes [15]. The chemistry of transition-metal, non-metal cluster compounds has undergone rapid developments; the activity has been particularly high for metal-Chalcogenide clusters [16-17]. Compounds which contain bond between transition metal and group-16 elements (S, Se, and Te) are studied because these main group elements act as bridges between different metal atoms in clusters and also as stabilizing ligand which prevent their fragmentation. These types of clusters are less explored than sulfur-containing cluster. Fig.2a shows an iron-molybdenum Chalcogenide cluster containing two Fe- atoms and two Mo-atoms bonded to S and Te. Mo atoms are also bonded to two Cyclopentadienyl ring and carbonyl groups. This cluster has been synthesized by the reaction of $Fe_3STe(CO)_9$ and $Cp_2Mo_2(CO)_6$. [18]. A sulphur bridged cluster, $[Mn_4Ni_2S_4(Cp)_2(CO)_{14}]$ has been shown in Fig. 2b, contains two Mn-Ni metal metal bond [19].

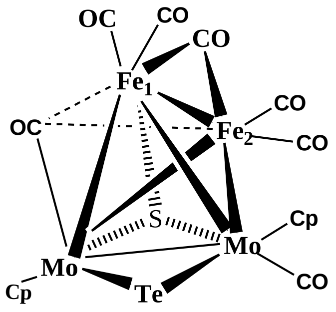


Fig 2a

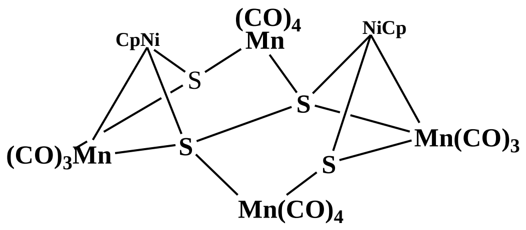


Fig 2b

Transition metal carbonyl compounds containing main group elements act as bridging ligand and are of great interest now a day [20]. Of the three group-16 elements S has the most extensive use in the cluster growth reactions. S exhibit diverse bonding modes in cluster. Clusters containing Se and Te in different bonding modes are also reported [21]. The bridged chalcogen atoms form a part of the cluster core so their variation can give rise to interesting changes in electrochemical behavior and other properties of the clusters. Some of the Se and Te containing metal clusters are shown in Fig.3 –Fig.5 [22, 23, 24].

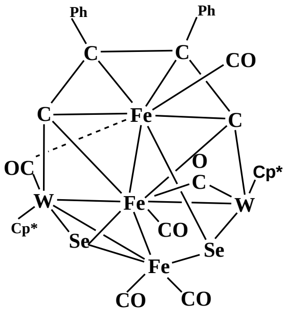


Fig 3

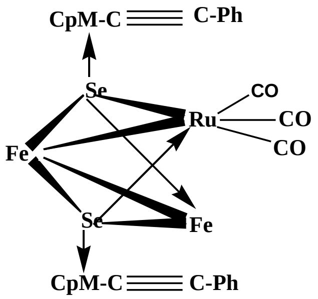


Fig 4

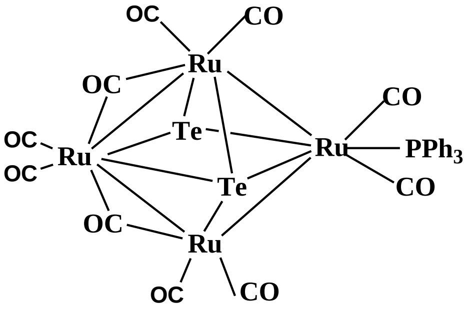


Fig 5

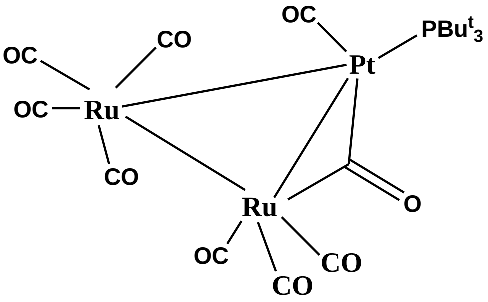
1.6 Transition metal cluster containing phosphine:-

Phosphine ligand binds well to most of the transition metals, especially those in the middle and late transition metals which include group 7-10 [25]. In terms of steric hindrance, PPh_3 is in intermediate between P (C_6H_{11})$_3$ and P (CH_3)$_3$. Metal clusters containing phosphine is one of the ligand that plays a vital role in stabilizing higher nuclear cluster. The phosphine ligation in metal cluster leads to variety of structural features and their unique reactivity. Some of the phosphine are used to bridge between two or more metal cluster to form a metal fragments. The technique used for the characterization for metal cluster containing phosphine is ^{31}P NMR spectroscopy.

There are two types of bonding mode in metal cluster containing phosphine as:-

1. **Monodentate phosphine binding mode:**

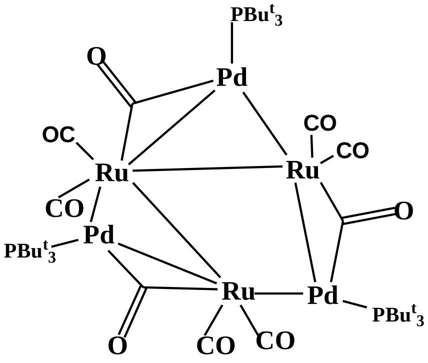
   Here only one phosphorus atom in the ligand binds to the metal, so the denticity is equal to one and the ligand is said to be Monodentate or unidentate.



$Ru_2(CO)_9[Pt(PBu^t_3)]$

Fig 6

This compound contains two ruthenium atoms joined by a Ru-Ru single bond= 3.0114 Å. There are also two Pd (PBu^t_3) groups that bridge the two ruthenium atoms on opposite sides of the molecule. The ruthenium atom, Ru (2) has five carbonyl ligand, four of which bridge to the neighboring Pd- atoms. Ru (1) has four carbonyl ligand, all of which are terminally coordinated. Ru (2)-Pd bond distances are shorter than Ru (1)-Pd bond distances. The shortness of Ru (2)-Pd bonds is due to the presence of bridging carbonyl ligand on those bonds [26].



$Ru_3(CO)_{12}[Pd(PBu^t3)]_3$

Fig 7

These ligand exhibit high enantioselective hydrogenation reactions. The heterometallic nanoparticles containing Pd or Pt exhibit better catalytic properties than the individual component. This is a heteronuclear cluster complexes bridging M(PBu^t_3) groups across metal-metal bonds [26].

Bidentate phosphine binding mode:

A ligand that binds through two sites is classified as bidentate ligand. They are also Lewis bases that donate two pair of electrons to metal atoms. They are referred to as chelating ligand.

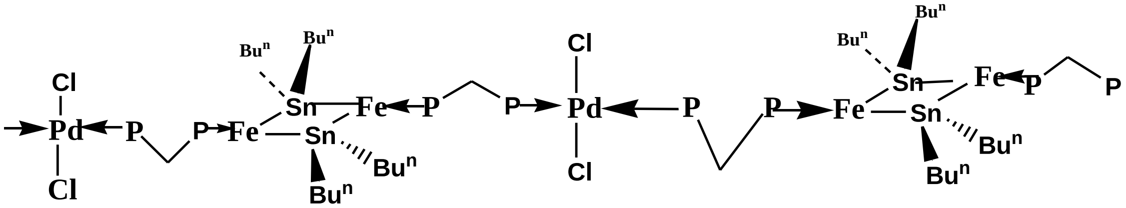
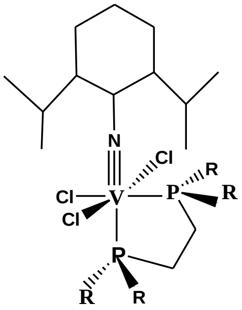


Fig 8

A new tetra nuclear FePdFeSn four-membered ring cluster, is viewed as a bent chain complex FePdFe bridged by a stannylene ligand. Here, a silyl ligand is considered as a protecting group. The uncoordinated phosphorus lone pair can be used for metal complexation. A palladium educt with two labile ligands is used to lead to an inorganic cyclic or linear polymer. It is rhombus like molecule with Pd, two Fe, four P-atoms are coplanar [27].



[V(N-2,6-$^iPr_2C_6H_3$)Cl_3(P-P)]

Fig 9

This type of cluster is prepared by addition of bidentate phosphine (dppe) to THF solutions of [V(N-2,6-$^iPr_2$C6H$_3$)Cl_3(dme)] to give the above complexes. It is an orange coloured solid. Here P- atom occupies the trans position with respect to the arylimido ligand. X-Ray analysis shows a pseudo-octahedral geometry with a meridional arrangement of the chloride ligand. The dppe ligand is non-symmetrically coordinated to the metal atom [44].

1.7 Chalcogenide metal cluster containing phosphine:-

Mixed metal clusters are of interest because of their application as precursors for the preparation of bimetallic and multimetallic heterogeneous catalysts. The synthesis of mixed-metal cluster complexes by the process of metal-metal exchange usually involves a sequence of two steps, consisting of a metal addition followed by a metal elimination [28]. The chemistry of transition-metal, non-metal cluster compounds has undergone rapid developments; the activity has been particularly high for metal-Chalcogenide clusters [29-30]. Mixed metal cluster complexes produce more intimately mixed bimetallic heterogeneous catalysts [31]. Variety of di- and polynuclear metal cluster complex is prepared in couple of decades [32]. Metal carbonyl chalcogenide cluster display unusual structures and reactivity patterns. Tellurium or Selenium containing iron carbonyl clusters deals with the synthesis and chemical reactivity of the anionic clusters and some neutral clusters. Ligand substitution reactions form an interesting aspect of the overall study of reactivity in mixed-metal clusters. Variation of the chalcogen atoms in the cluster amongst the congeners S, Se and Te, could lead to interesting contrasts in the reactivity of the ligand substitution reactions. According to Rauchfuss et al., the tellurium containing clusters have structural features and reactivity which are different from those of sulfur or selenium analogues [33].

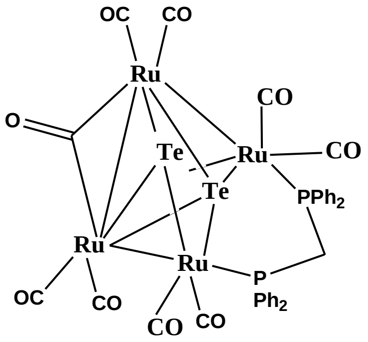


Fig. 10

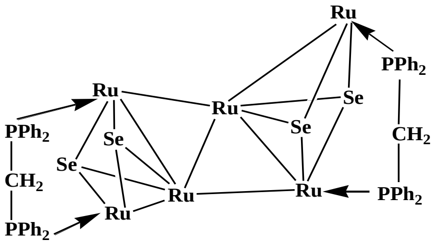


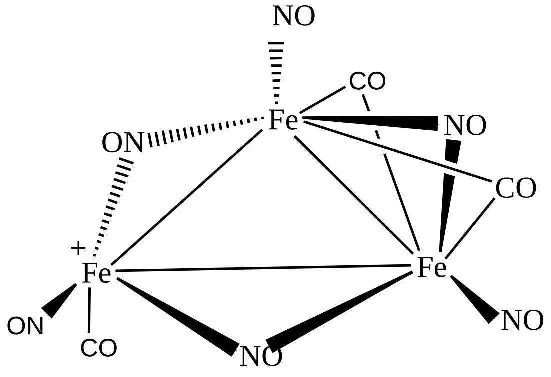
Fig. 11

In Fig. 10 & 11 the chalcogen forms the internal core of the structure while dppe ligand forms the outer portion the core. They are bridged to the metal and chalcogen to form a higher nuclear cluster [34, 35]. The chemistry of transition- metal selenido and tellurido mono and poly-nuclear complex is of increasing interest because this ligand are useful in cluster growth reactions and precursors in inorganic solids with novel electronic, magnetic and optical properties [36].

1.8 Types of metal clusters:-

Clusters are of following types:-

1. Polynuclear carbonyls, nitosyls [37].



$Fe_3(NO)_8(CO)_3^+$

Fig 12

2. Metal halides and oxide complexes.

   Metal atoms in the first class have low formal oxidation state -1 to +1, while those in second classes is found in higher oxidation states, +2 to +3.

   Class-1 clusters are typically made up of late transition metals, while class-2 metals are made up of early transition metals.

3. Binuclear metal clusters:-

   Multiply bonded M-M dimmers with bond orders up to 4 are most common binuclear metal cluster compounds. $Re_2X_8^{2-}$ ion (X= Cl^-, Br^-) and binuclear carboxylates $M_2(O_2CR)_4$ (M= Cr, Mo, W, Re or Ru). Fig.13 shows the structure of Octachloridirhenate(III) ion.

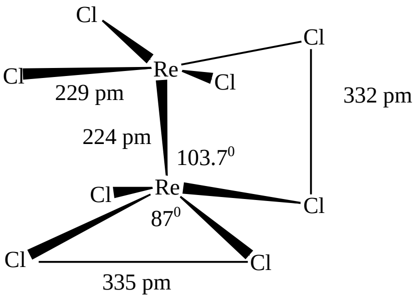


Fig.13

4. Trinuclear metal cluster:- The noncarbonyl cluster containing three metal atoms are the rhenium trihalides $[(ReCl_3)_3]$ and their derivatives. Here each rhenium atom is bonded directly to metal-metal bonds and indirectly by a bridging halogen ligand.

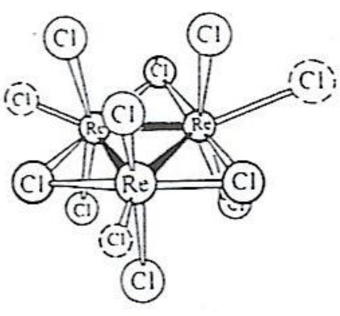


Fig 17: $[Re_3Cl_9]$

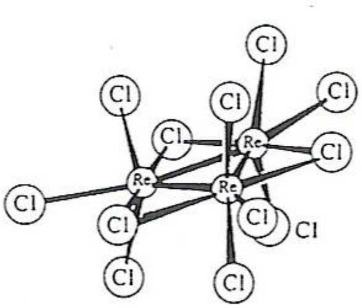


Fig 18: $[Re_3Cl_{12}]^{3-}$

Trinuclear cluster are formed by early transition metal in their low oxidation state. The basic structure for this type is known as (M_3X_6) without μ_3 ligand, (M_3X_{13}) type with one μ_3 ligand and (M_3X_{17}) type with two μ_3 ligand.

According to geometry cluster are of following types:-

Triangular $[M_3X_9L_3]$ type: - $[Re_3Cl_{12}]^{3-}$

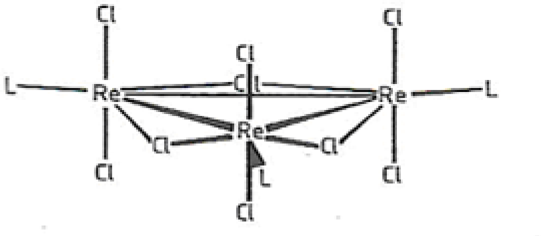


Fig 19: $[Re_3Cl_{12}]^{3-}$

5. Tertranuclear metal clusters:- Some tetranuclaer cluster are reported in form of carbonyl clusters and some as halides and oxide compounds.Fig 14 shows a tetranuclear molybdenum cluster containing chloride and phosphine ligands.

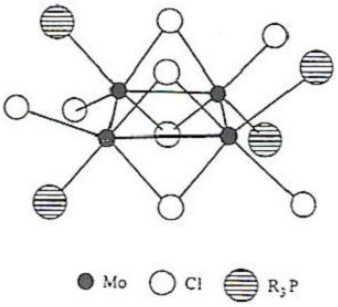
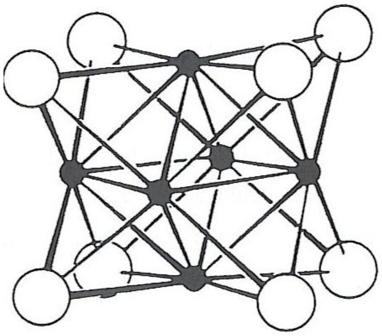


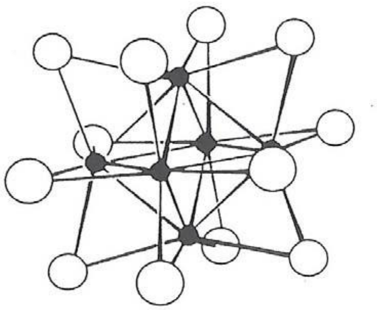
Fig 14

6. <u>Hexanuclear metal clusters</u>:- These hexanuclear metal clusters contains six metal atoms. These types of clusters containing Molybdenum, Niobium, and Tantalum were earlier known. There are two types of hexanuclear clusters:
    a. In one type the six molybdenum atoms form an octahedral structure. Eight chloride ligand bridge three of the six metal atoms.
    b. Other type also contain an octahedron of metal atoms, but there are twelve halide ligand along the edge of the cluster.



$[M_6X_{12}]^{2+}$ X= Cl, Br

Fig 15



$[Mo_6Cl_8]^{4+}$

Fig 16

1.9 Types of cluster catalysis:-

Cluster catalysis is of three types as follows:-

1. Homogeneous, relatively low-nuclearity clusters that are soluble in solvents.
2. Heterogeneous, insoluble cluster networks or colloids that can be suspended in a solvent.

3. Heterogeneous, relatively high-nuclearity nanoparticle that can be either clean surface or surface-ligated supported or free.

1.10 Catalytic Activity of Metal clusters:-

Catalysis by metal is a surface phenomenon. Many technological catalysts contain small supported metal particles with a large fraction of particles exposed [38]. Reaction like hydrocarbon-hydrogenation is structure insensitive, proceeding at same rate on metal particles and also shows bulk-like metallic behavior [38]. The possibility of tailoring the catalytic behavior of metal clusters is raised by controlling the cluster size. Metal cluster can function as catalysts of reactions that are not affected with mononuclear coordination or organometallic complexes. There are two types of reaction involved in catalysis as:- Hydrogen reduction of molecules with triple bonds like N_2 and CO [39]. The more thermally stable metal carbonyl clusters like Os_3 (CO) $_{12}$ and Ir_4 (CO) $_{12}$ catalyses very slowly the hydrogen reduction of CO to CH_4 [40]. A tetra nickel atom cluster binds and also activate for a reduction reaction like molecule and ions with triple bonds. E.g. RCN, RNC. The catalytic chemistry base of the metal cluster-metal surface analogy to hydrocarbons was successful for metal carbonyl clusters. Some reactions are cyclohexadiene disproportionation to benzene and cyclohexene. The use of metal cluster compounds, especially as catalysts has grown steadily.

1.11 Use of metal cluster:-

Solution of novel macromolecular structure is done by a variation of heavy-atom method, utilizing the X-ray scattering properties of a small number of heavier atoms. In SIR or MIR approach usually heaviest atom are used and the derivatization reagents include elements from the last row of the periodic table such as Pt, Au, Hg, U as $PtCl_6^{2-}$, $Au(CN)^{2-}$, HgI_4^{2-}, UO_2^{2+}. It is advantageous to have several heavy atom sites for phasing structure of larger proteins. The proteins crystals can be incorporated into multiple heavy atoms is to utilize the clusters containing several metal atom bound together and a large number of scattering electrons are provided. Several proteins involved in the redox or electron transfer pathways contain natural multi-atom clusters of transition metals such as Fe, Ni, Cu, Mn, Mo. The intrinsic metal can be used for phasing crystal structures of such proteins, based on their anomalous scattering properties. The use of metal clusters offers a way of introducing to proteins crystals multiple-heavy atom sites, enhancing the phasing signal. At low resolution when the individual metal positions are not resolved, the whole clusters acts as “super atom”. Because of their high phasing power at low resolution the polynuclear metal clusters have been used for crystal structures of large proteins or their multicomponent complexes.

Potential use of some metal clusters as hydrogen storage materials:-

A global boom in population has led to several social and environmental problems for the human race. Excessive use of fossil fuel has made a deep impact on natural energy reserve. Use of solar cells as non-conventional energy resources has been employed. Hydrogen, the third most abundant element on earth is an environmental friendly energy carrier in the automobile industry and also a good substitute for fossil fuel resources. Due to lack of appropriate materials for physical storage of hydrogen is the primary reason for the limiting gases. The stability of the hydrogen trapped complexes also achieves some thermodynamic support from the negative change in energy values. So all these metal cages and rings are applied as trapping materials for hydrogen - which is a future fuel reserve

Phosphines are important ligand in coordination chemistry especially in organometallic compounds [41]. They stabilize low oxidation states of metal centers. They are three coordinate phosphorus compounds(R) where each group has C-atom attached to Phosphorus. They are pyrrophoric, sensitive to oxidation of air. It has a pyramidal geometry. Metals of group-VIII are usually known as active catalysts. Phosphine (PH_3) is the simplest compound used in transition metal chemistry. Triphenyl phosphine $(C_6H_5)_3P$ is most stable. Phosphines are Lewis bases since they possess lone pair of electrons. The lone pair is donated to metal to form a complex. The P-M bond is strengthened by back-bonding involving donation of electrons from filled metal orbital to empty phosphorus d-orbital. These complexes have low oxidation states.

The metal-phosphine complex show oxidative addition reactions. The term oxidative addition is the reaction of metal complex with neutral covalent molecules in which neutral molecule is added to the complex and is not itself not oxidized, e.g. $[Ir(CH_3)(Cl)(I)(C_6H_5)_3P]$ [42,43].

The phosphine exchange reactions are used as a synthetic route for preparation of complexes from triphenyl phosphine complexes. The addition of phosphine which is more basic than triphenyl phosphine displaces the coordinated $(C_6H_5)_3P$. The ligand in metal-phosphine complexes act as Lewis bases (electron donors). The donation of electrons from the phosphorus atom to the metal have greater positive charge on the P and thus enhances the electron-withdrawing properties of complexes with respect to the aromatic ring.

The phosphine ligand function as electron acceptors from metal if metal-ligand π-bonding is present. This type of bonding decreases the positive charge on Phosphorus (P). The oxidation state plays an important role in stability of the complexes. Metals in low oxidation state are stable when they form complexes with ligand such as CO, which is capable of accepting as well as donating electrons, while high oxidation states complexes are good donors and don’t oxidize itself. The maximum stability is obtained when the donor and acceptor properties of ligand are matched with those of the metals. Most stable complexes require considerable activation energy. For attaining maximum stability, aryl phosphine complex are better donor group, while alkyl phosphine are better accepting group. The donor abilities of halides decreases in the order: $I^- > Br^- > Cl^-$.

Attempts are made to synthesize and characterize different homo- and hetero-metallic clusters which are having novel properties. But our interest focuses on to synthesize higher nuclear heterometallic cluster stabilized by main group elements like S, Se, and Te to stabilize transition metal clusters. The compound like $[Fe_3(CO)_9(\mu\text{-}E_2)]$ and $[Fe_3(CO)_8(PPh_3)(\mu\text{-}E_2)]$ (E= S, Se, Te) have been used as a convenient starting materials for several cluster growth reactions.

Ligand which are attached to metals are also important to maintain the cluster geometry. The carbonyl ligand is one of the most common ligand in metal cluster and it is unsaturated due to C-O bonds. These ligand acts as π-acceptor by accepting d-electron by the metal through back-donation. Thus CO acts as a spectator ligand.

Other types of ligand are also used in metal cluster reactions like triphenyl phosphine (PR_3). The use of phosphine ligand is important in all homogeneous catalysis with precious metals. Phosphine ligands are strong σ-donor ligands and weak π-acceptors. The electron-donating group decreases the effect, but electron-withdrawing group increases the π-acceptor backbonding. The chiral information is mostly provided by the phosphine ligands together with the catalytic activity of the suitable precious metal. Chelating ligands like $Ph_2P(CH_2)_nPPh_2$ (dppm, dppe) enforces a cis arrangement of the chelate effect.

2.2 Results and Discussions

The Tellurium compound, $[Fe_3Te_2(CO)_9]$ (**1**) was stirred with equimolar amount of DPPE (Bis-Diphenylphosphino-ethane) in dichloromethane solvent for 24 hr at room temperature in presence of N_2 atmosphere. After the reaction was over, one major product (**2**) and three minor products (**3-5**) were separated using preparative TLC. The separated products (**2**-**5**) were characterized by FTIR spectrum, which shows the presence of terminal bonded metal carbonyl groups. Compound **2** was structurally characterized by single crystal X-ray crystallography. The structure reveals the presence of two Fe_3Te_2 unit linked together by dppe ligand. Each Fe_3Te_2 unit has one Fe-Fe bond and six Fe-Te bonds. Each iron atom is attached to three terminally bonded carbonyl groups satisfying the electron counting.

The phosphine substituted tellurium bridged cluster $[Fe_3Te_2(CO)_8(PPh_3)]$ (**6**) was stirred with equimolar amount of DPPE (diphenylphosphinoethane) in dichloromethane solvent at room temperature in presence of nitrogen atmosphere, to obtain an orange coloured product (**7**). Compound **7** has been characterized by FTIR spectrum which reveals the presence of terminal bridging carbonyl ligand with v_{CO} in the range of 2000-1950 cm^{-1}. The Infrared spectrum was compared with literature value to establish the probable structure of compound **7** [33].

3. Conclusions

The chemistry of tellurium containing iron carbonyl clusters has been interesting synthetically and structurally. Tellurium bridged tri-iron metal cluster with bridging phosphine ligand was synthesized and characterized by FTIR, Single-crystal X-ray diffractometer. Reaction of different types of triiron telluride cluster with diphosphines led to the isolation of two types of cluster framework. One containing two cluster fragment linking together to form a higher nuclear cluster (**2**) and another has intramolecular briged diphosphine unit (**7**). In both the compounds the bis (diphenylphosphino-ethane) act as bridging unit between metals. Thus, stable cluster containing both diphosphine and tellurium bridging iron clusters have been synthesized in high yield.

4. References

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