

Research Article

The Role of Ligands, Polytopic Ligands and Metal Organic Ligands (Mols) in Coordination Chemistry

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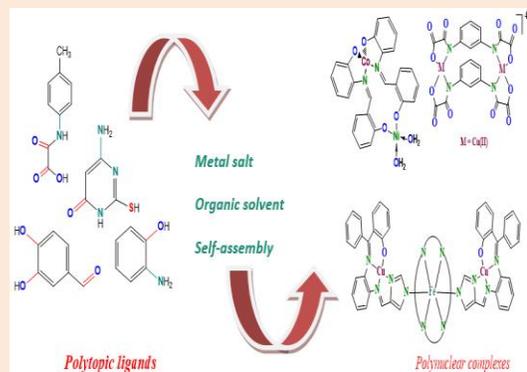
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Abstract

This mini-review discusses the different types of ligands, polytopic ligands and metal organic ligands (MOLs) of 21 years with particular focus on the one pot synthesis of different homo and hetero polynuclear complexes using MOLs. Amongst the different methods used for the synthesis of polynuclear complexes the complexes used as ligand is the most successful method. The properties of complexes originating due to metal ions may get enhanced in polynuclear complexes. Moreover, the interaction between the metal ions in such complexes may give rise to new properties. The tailor made polynuclear complexes synthesized by suitable methods with expected structure and properties can be applied in different fields.

Keywords: Polytopic ligands, polynuclear complexes, molecular organic ligands, ligands.



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Introduction

Coordination chemistry, the science concerned with the interaction of organic / inorganic ligands with metal centers has remained one of the most active research areas in inorganic chemistry. Coordination chemistry includes different types of coordination compounds applicable in a wide diversity of fields such as dyes, colors, nuclear fuels, catalysis, photography, toxicology, bioinorganic chemistry, medicine, ceramics, materials science and toxicology. Inclusion of a variety of ligands in complexes has enabled their applications as biocides, catalysts, NMR shift reagents and DNA binders [1, 2]. The development of sophisticated analytical instruments and synthesis of a wide variety of coordination compounds has encouraged many researchers to revisit the chemical reactions. This study has enabled the inorganic chemists to make significant progress in the modification of the concept of chemical bonding [3].

In coordination chemistry, the different types of ligands, Schiff base ligands and chelates are well documented with synthesis, characterization and applications [4]. The complexes of transition metals with higher nuclearity have attracted the attention of many coordination chemists, where polytopic ligands are important for tailor made molecular structures of complexes. The polytopic ligands are much better for the successful preparation of the homo polynuclear complexes whereas, the one-pot synthesis for the preparation of polynuclear complexes is very complicated [5-10]. In order to facilitate the tailor making of heterometallic systems in a controlled manner and with expected properties, the greatest concern is the development of synthetic routes. From amongst the variety of methodologies, the use of metal complexes as ligands has proven to be very successful. If the complexes formed by coordination with metal ions, have the tendency to coordinate further or react with other complexes, then they may act as 'metal organic ligands' [11-17]. The different types of MOLs (metal organic ligands) which form various homo and hetero polynuclear complexes are reported here. The polynuclear complexes are very useful in different fields, especially used as magnetic materials. Nowadays, magnetic materials are being used in biomedical applications such

as contrast agent in magnetic resonance imaging (MRI), targeted drug delivery and magnetic separation of cells, DNA, protein etc [18,19].

Ligands, Schiff base ligands and chelates.

Ligand is the species attached to a central metal atom / ion to form a coordination complex. The ligand is the electron rich compound with extra electrons. The nature of metal – ligand bonding can be covalent or ionic [14]. Ligands can be anions, cations or neutral molecules. According to the number of donating atoms, the ligands may be bidentate, tridentate or polydentate. Examples of some ligands are given in (**Figure 1**).

The condensation of primary amines with aldehydes or ketones gives compounds with a functional group that contains a carbon-nitrogen double bond with the nitrogen connected to an alkyl group (**Figure 2**). These are called Schiff bases, since their synthesis was reported by Hugo Schiff (1864) [20].

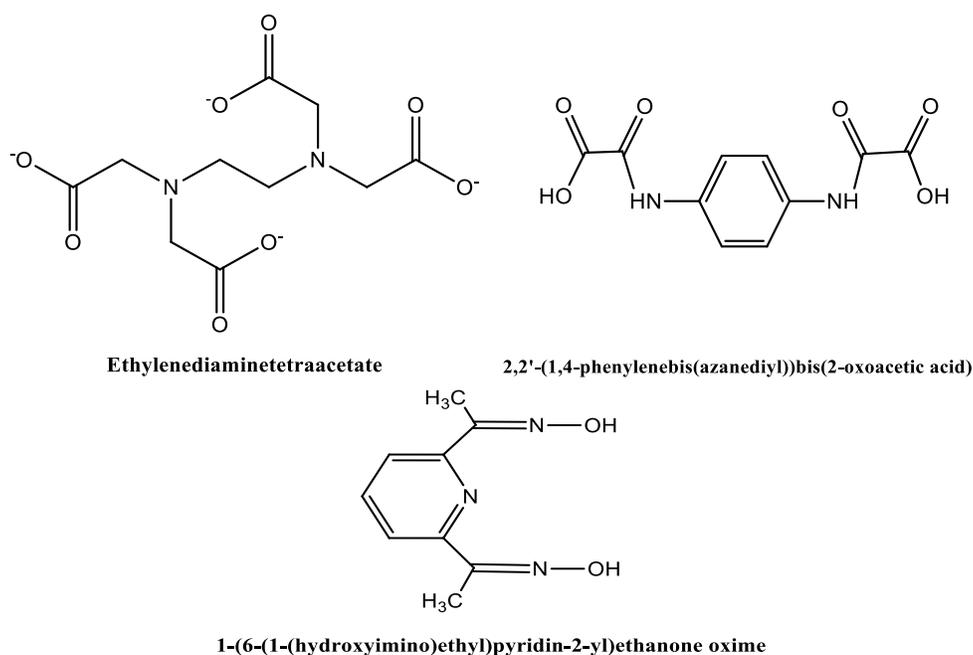


Figure 1 Different ligands



Figure 2 Schiff base ligands

The process in which polydentate ligand bonds to a metal ion, forming a ring structure or complex structure is called chelation. The polydentate ligand is referred to as a chelating agent and the complexes involving a ring in which metal ion is an integral part is called a chelate. Ethylenediaminetetraacetic acid (EDTA) is a popular hexadentate ligand in coordination chemistry with four carboxylic acid groups along with two amine groups can form six bonds with a metal ion. EDTA forms chelates with a wide variety of metal ions under suitable conditions which contain five 5-membered rings in their structure. The hexacoordinated complexes from EDTA are octahedral in geometry (**Figure 3**).

Polytopic ligands

In recent years in coordination chemistry, much focus has been placed on the synthesis, characterization and applications of dinuclear and polynuclear transition metal complexes bridged by polyatomic ligands [5].

The behavior of single metal ions embraced by a monodentate as well as the chelating ligand environment has been studied extensively to date. In such systems, individual metal centers are usually too far from each other which restricts the possibility of spin-spin coupling between paramagnetic metal ions [21]. Polytopic ligands range from ditopic to hexatopic displaying different geometry and length, can be designed in such a way that the synthesis becomes convenient. They may also contain a variety of functional groups; such a rich library of ligands gives an opportunity to systematically study the relationship between the geometry of the ligand and the functionality of the product obtained. Some examples of the polytopic ligands with hard coordination functions containing oxygen and/or nitrogen as donor atoms are discussed here [22, 23].

Diketones

The classical β -diketones and related ligands have been studied for more than a century give rise to rich and interesting coordination chemistry. The powerful β -diketones act under appropriate conditions as nonnegative O_2^- chelating donors, capable of stabilizing mononuclear or polynuclear complexes. Their keto-enol tautomerism has been studied in solution by IR and NMR spectroscopy and in the solid state by X-ray single crystal diffraction (**Figure 4**) [24].

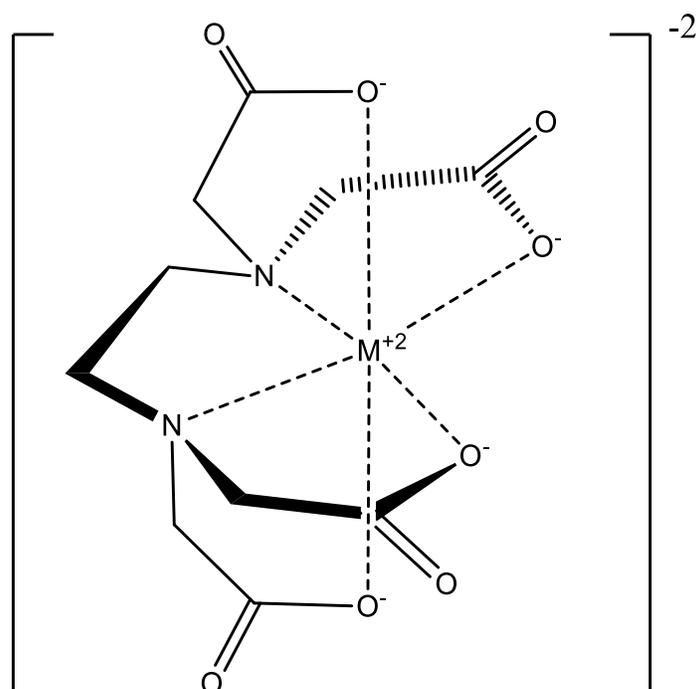


Figure 3 Chelated complex of EDTA

There is a growing amount of literature which especially deals with the possible applications of these complexes in electroluminescent devices for light emitting diodes, NMR shift reagents and magnetically addressable liquid crystals [25].

Here, the increasing number of carbonyl groups with the resulting formation of tri- or tetraketones and bis- β -diketones (**Figure 5**) allows the formation of well-defined homo- and /or heteropolynuclear complexes.

The complexes prepared from poly-diketones have extraordinary physico-chemical properties, arising due to the coordination of identical or different metal ions in close connection and interacting with each other through the carbonyl bridges. Likewise, the interesting series of β -ketophenolate generated by inclusion of phenol groups at the end or between the carbonyl moieties (**Figure 6**), capable of securing up to eight metal ions in close proximity [26].

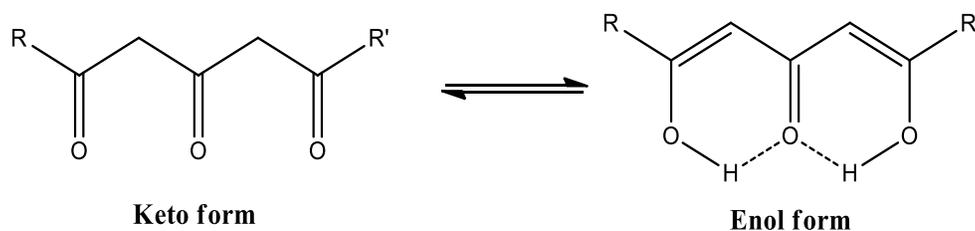


Figure 4 Keto-enol tautomerism in diketones

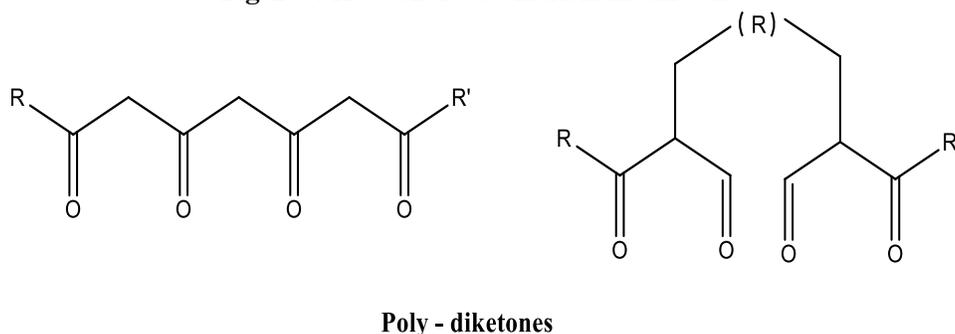


Figure 5 Poly-diketones

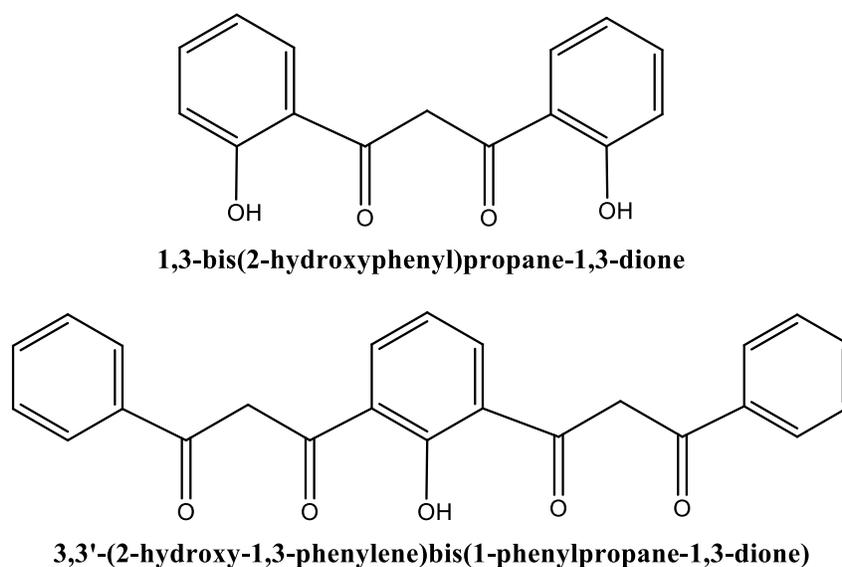


Figure 6 Keto-phenol derivatives.

Dicarboxylates

The anion of dicarboxylate anion is capable of generating homo- and heteropolynuclear complexes. Due to the outstanding flexibility of the oxalato ligand there is a wide structural diversity in the oxalato-bridged complexes (**Figure 7**). The oxalate ligand is the simplest dicarboxylate. The oxalate bridge formed by oxalate ligand can strongly mediate the exchange interactions between the paramagnetic metal ions and shows interesting magnetic properties [27].

Several oxalato-bridged homo and polynuclear complexes have been synthesized and characterized to date. These compounds are generally obtained through the reaction between cationic complexes having potentially free coordination sites and the oxalate anion [28].

Phenolic ligands containing one or two phenolic units

In 1970, Robson defined a class of ligands able to form di- or polynuclear metal complexes by simultaneously attaching to two or more metal ions. The phenol-based molecules have attracted the greatest attention of a great number of researchers from amongst the many different types of dinucleating ligands and polynucleating ligands [29]. This is due to the key role played by the phenolic group which has many useful electronic and structural characteristics. The phenolic ligands can have different nucleating arms, including phenolic group.

The ligands with one phenol unit have appeared as an important class of acyclic ligands capable of binding two metal ions close to each other in addition to bridging abilities of the phenolate oxygen atom towards metal ions whereas, the ligands with two phenolic groups can form dinuclear as well as polynuclear complexes. Some of the phenolic ligands containing amine or polyamine side arms (**Figure 8**).

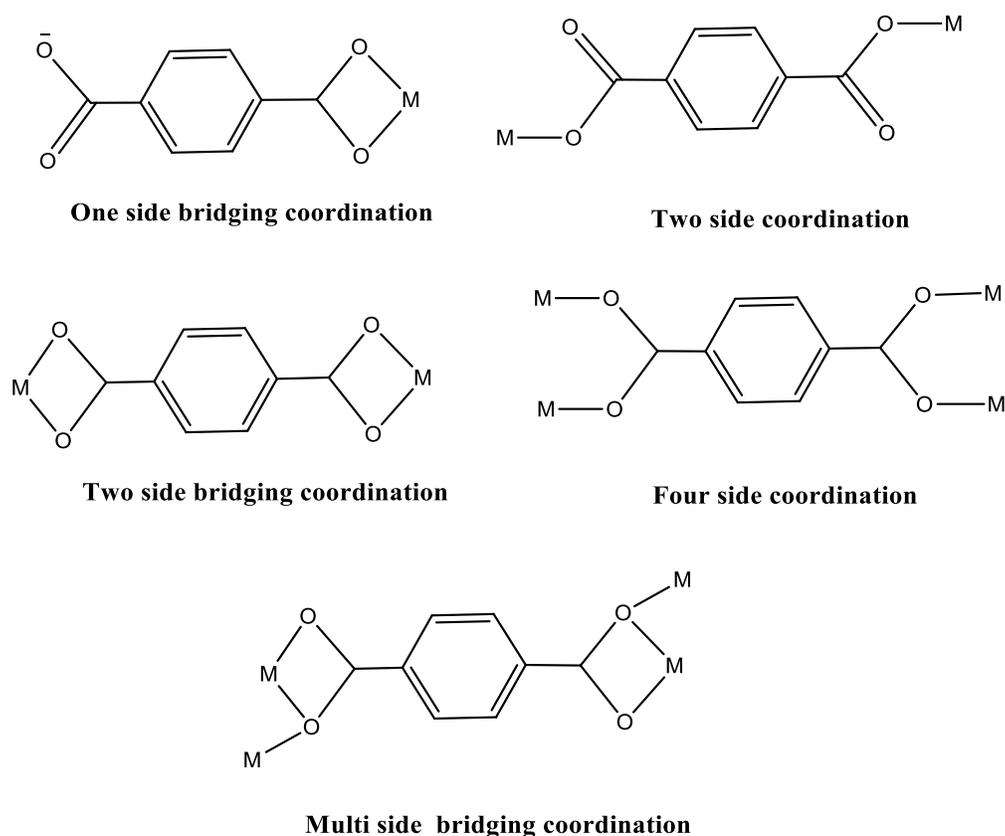


Figure 7 Modes of coordination of dicarboxylates.

Some ligands containing one phenolic unit with a reactive group (an aldehyde) can react with diamines to form the Schiff base ligands with polynucleating atoms. Schiff base reaction of o-vanillin and benzidine form the Bis (o-vanillin) benzidine (**Figure 9**) which can generally used for the formation of homonuclear complexes.

Metal organic ligands (MOLs)

The mononuclear transition metal complexes prepared from monodentate as well as polydentate chelating ligands have been studied extensively, but in the last twenty five years, complexes of transition metals with higher nuclearity have attracted the attention of many coordination chemists. This class of compounds is found with several names such as oligomeric complexes, polynuclear complexes, cages and clusters [30]. For the synthesis of polynuclear complexes, a central question arises: 'Are there any universal methodologies for the template synthesis of polynuclear complexes?' The general answer of this question is 'No'.

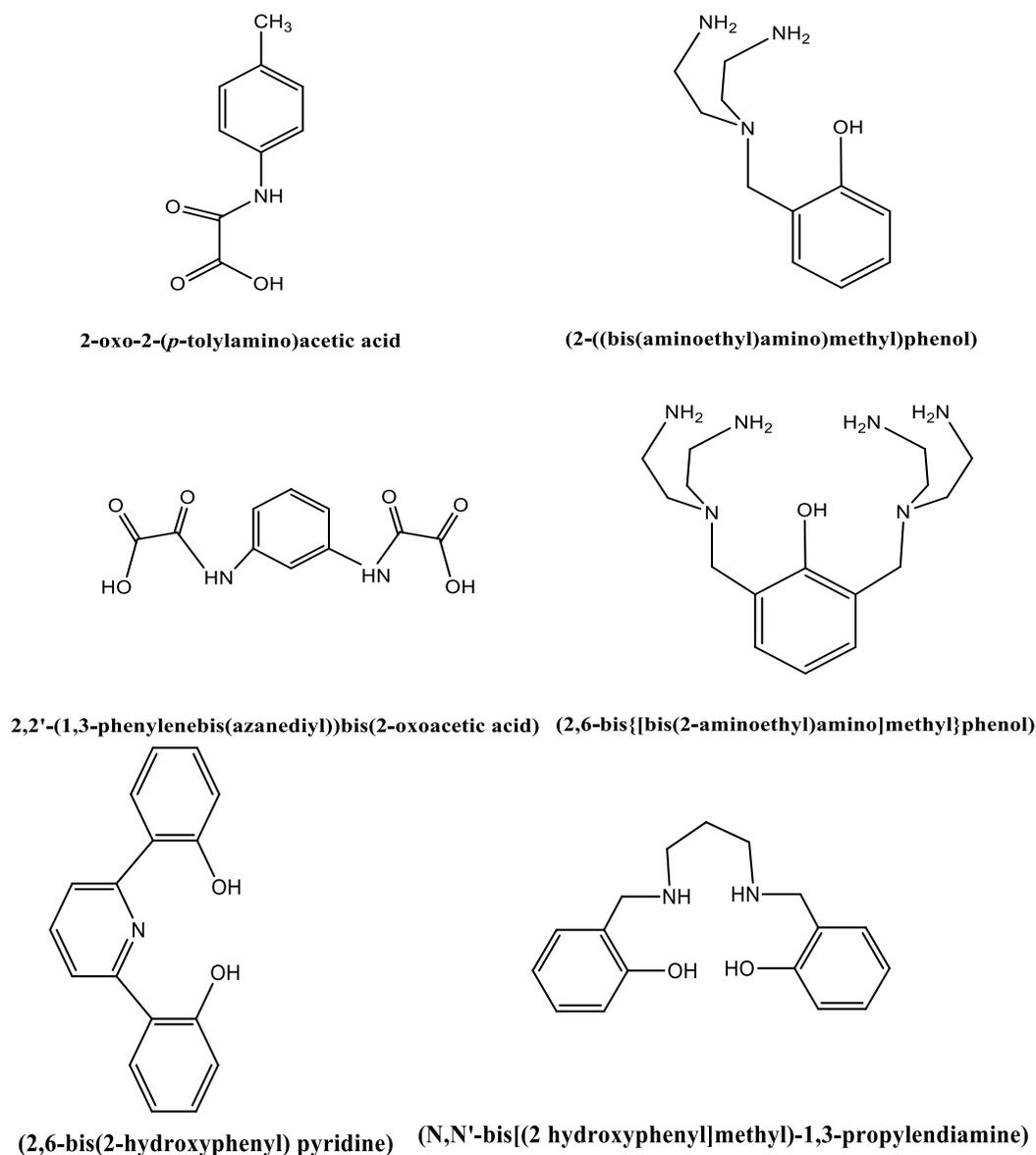
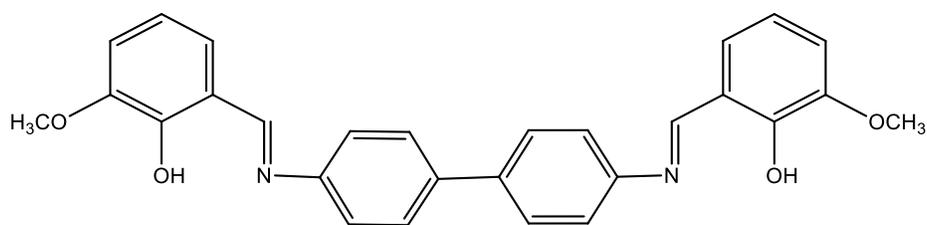


Figure 8 Ligands containing one or two phenolic units



Bis (o-vanillin) benzidine

Figure 9 Phenolic Schiff base ligand

In organic chemistry there are the predictive synthetic schemes and routes, whereas in contrast to that, polynuclear transition metal chemistry cannot be described as operator controlled. In order to facilitate the tailor making of polynuclear complexes with high nuclearity, particularly heterometallic systems in a controlled manner and with expected properties, the greatest concern is the development of synthetic routes [31]. From amongst the variety of methodologies applied to synthesize polymetallic coordination compounds, the use of ‘metalloligands’, i.e. metal complexes as ligands, in which the ligands are already bound to one metal and have free coordinating sites that can bind a second metal of the same or a different kind has proven to be very successful [7]. Different complexes containing one or more metal centers are able to react further with other complexes through available appropriate donor atoms as well as reactive groups. One should begin with monometallic precursors which can react chemically to form polymetallic complexes. These types of complex precursors are considered as ligands and named as metal organic ligands (MOLs) [32]. The well recognized approach of ‘metal complexes as ligands’ involving multinucleating ligands offers many probable advantages over the self-assembly route and it enables greater control over the route of the reaction and the products. The MOL approach allows the synthesis of complexes with higher nuclearity by reaction of mono or binuclear complexes of appropriate ligands [33]. These approach using polynucleating ligands proceeds gradually and provides a means to gain control of the nuclearity in addition to the preparation of species containing different metal ions, i.e. heterometallic complexes. Thus, in this manner, it is possible to build polymetallic systems in a stepwise fashion having both homo and hetero-variants [34].

Homopolynuclear complexes

The homopolynuclear complexes synthesized by polytopic ligands allows the coordination of metal ions through the reactive groups having donor atoms such as nitrogen, oxygen or sulfur. This self-assembly approach allows the rational preparation of linear double- and triple-stranded oligonuclear complexes from mono- to di- and trinuclear species [3]. The preparation of complexes depends on the molecular symmetry, coordination mode of the polytopic ligands and the preferred coordination geometry of the metal ions (**Figure 10**).

The polynuclear complexes are prepared for the different purposes. The synthesis of molecular magnetic materials requires an intelligent design of the ligand which can organize the paramagnetic metal ions in a desired topology and efficiently transmit electron exchange interactions between the metal ions. This basic principle is strongly supported by the work on the magnetic properties of oxamato – bridged multimetallic coordination compounds which was initiated by Kahn and coworkers in the late 1980’s and then extended to the oxamidato – bridged analogues by Journaux and Lioret in the late 1990’s. In this work, as discussed earlier, aliphatic or aromatic group substituted bis(oxamato)- and related bis(oxamidato) – copper(II) complexes were used as ligands, referred to as metal-organic ligands (MOLs) for the preparation of multimetallic compounds [13, 32, 33].

The study of polynuclear complexes was initiated using the ligands like oxalates which formed the homopolynuclear complexes [7]. Since the 1990’s, a great number of oxalate-bridged homopolynuclear complexes have been synthesized and characterized to date. These compounds are normally obtained during the reaction between cationic complexes having potentially free coordination sites and the oxalate anion. These types of homopolynuclear compounds can be formed using the polytopic ligands. But, as discussed earlier, one of the challenges in the field of polynuclear self – assembly of molecular organic – inorganic material is the controlled and on the spot generation of

tailor made molecular structures and properties [35-37]. The high degree of structural organization can be achieved through the multiple one- to three- binding of transition metals. Hence, it is important to design the organic ligand together with the proper choice of the metal ion. The oxalate type ligands can be modified to ligands having bis-chelating coordination ability, the bridging oxalate type units have produced different types of frameworks, which include 1D-chains, 2D-layer and 3D-networks bearing the same types of metal ions [38-40].

Heteropolynuclear complexes

The synthesis of heterometallic complexes is known to be difficult. A one-pot procedure involving the reaction of two different metal ions with the ligand anion produces a mixture of compounds. In order to overcome this difficulty, an alternative synthetic strategy (metal organic ligands) has been developed which consists the use of mononuclear complexes as ligands towards the second metal ion [41].

Plenty of work on the well – recognized ‘metal complex as ligands’ approach has been done to date. The different researchers used different types of MOL for the preparation of homo and heteropolynuclear complexes. For the synthesis of tailor made molecular structures of the polynuclear complexes, the preparation of the MOLs is very important [42].

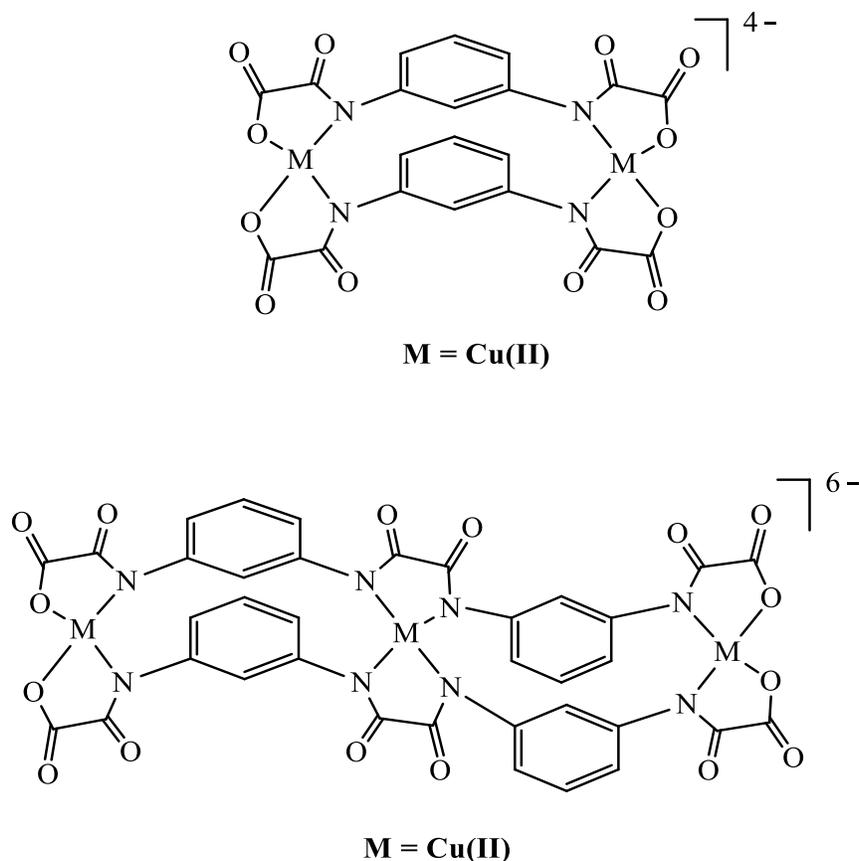


Figure 10 Homopolynuclear complexes

M.C. Dul and coworkers explained the molecular-programmed self-assembly of metal-organic ligands which have the free carbonyl oxygen. This free carbonyl oxygen allows self-assembled mono-, di-, and trinuclear square planar or octahedral complexes to be used as MOLs toward other metal ions ($M(\text{II}) = \text{Cu}, \text{Ni}, \text{Co}, \text{Mn}, \text{Fe}, \text{Zn}$) (**Figure 11**). This molecular self-assembly approach allows the rational preparation of polynuclear complexes as well

as coordination polymers with different nuclearity, topology, and dimensionality, depending on the coordination mode of MOLs and coordinated metal ions [5].

Synthesis of the homodinuclear complexes from ligand (**L**) by the reaction of sodium 2,6-diformyl-4-methylphenolate and 1,3-diamine propane (**Figure 12**) reported by H. Adams [43]. The Schiff base complex $[\text{Na}_2(\text{L})]$ formed readily undergoes transmetallation by $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ to produce $\text{Zn}_2(\text{L})(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$.

Whereas, the heterodinuclear complexes $[\text{M}_A\text{M}_B(\text{L})]^{2+}$, where $\text{M}_A = \text{Ni}^{2+}$, $\text{M}_B = \text{Mn}^{2+}$, Fe^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+} were prepared by two step synthesis, based on the reaction of metal acetates with mononuclear nickel complex. The first step of the reaction is the formation of mononuclear nickel complex; one of the coordination compartments was blocked by protonation of inner penalty groups. On other hand, in the second step acetate ions deprotonated the phenolate groups and made it available for the further coordination. So, by the modification of the synthetic method the homodinuclear and heterodinuclear complexes from same Schiff base ligands can be formed.

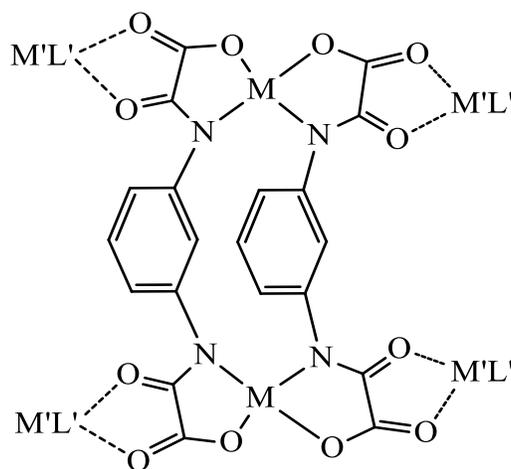


Figure 11 Heteropolynuclear complexes

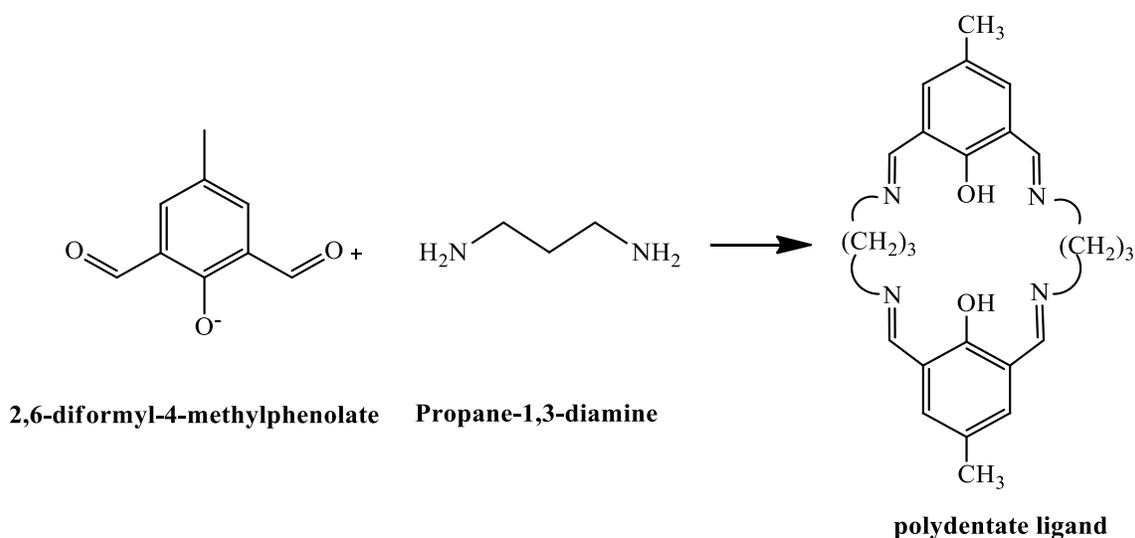


Figure 12 Polydentate ligand used for polynuclear complexes

E.Q. Gao and coworkers also used ‘complex as ligand’ approach to prepare polynuclear species. Many oxamido-bridged polynuclear complexes were prepared by using mononuclear Cu(II) complexes of some *N,N*-bis(coordinating group substituted) oxamides such as [Cu(oxpn)] and [Cu(obze)]₂ as ligands (**Figure 13**). The diamines and dioxalates are used for the preparation of the mononuclear complexes. The mononuclear complexes with free coordinating sites were used as MOLs for the preparation of the dinuclear complexes [44].

The mononuclear complexes (Figure 13) have free oxalate sites for the further coordination. The mononuclear complexes with variation of different ligands with the substitutions give different types of dinuclear complexes. The dinuclear complexes prepared from the above method are different from which they reported the dinuclear Cu(II)-M(II) (M=Cu, Ni, Mn) complexes (**Figure 14**) [45].

Some other types of metal organic ligands have been designed using a ligand containing number of potential sites from which all cannot contribute in the coordination but, the monotopic complexes formed from these types of ligands can act as precursors and further coordination occurs. The mononuclear complexes of transition metals prepared from 6-amino-2-thiouracil containing the amine group as unutilized functionality (**Figure 15**). These types of mononuclear complexes can be modified for further reaction to form the polynuclear complexes [46]. From amongst many methods for the preparation of polynuclear complexes, Y. Sunatsuki and coworkers implemented two methods. The first method (1) in which, one kind of metal complex contains simultaneous donor and the acceptor ability for the further coordination and construct the assembly structure. The second method (2) in which, two kinds of metal complexes contain simultaneous donor and the acceptor ability for the further reaction. The second method is successfully used in the preparation of molecular magnetic materials [47].

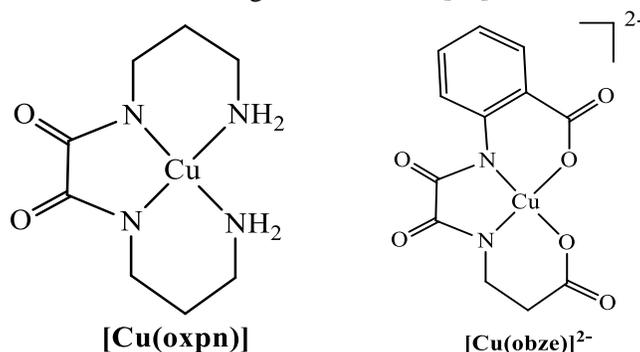


Figure 13 Mononuclear complexes used as MOLs

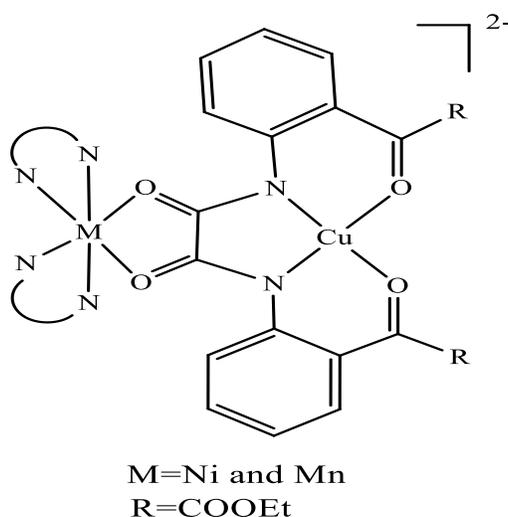


Figure 14 Dinuclear complexes of MOLs

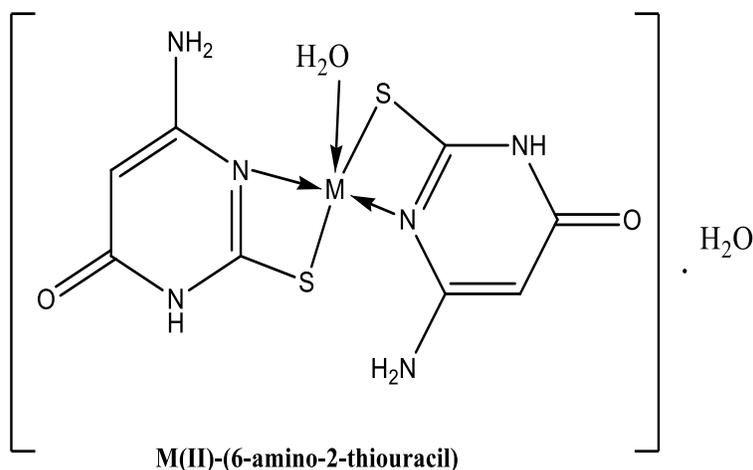
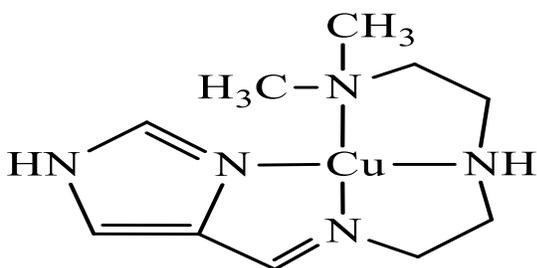


Figure 15 Mononuclear with active sites.

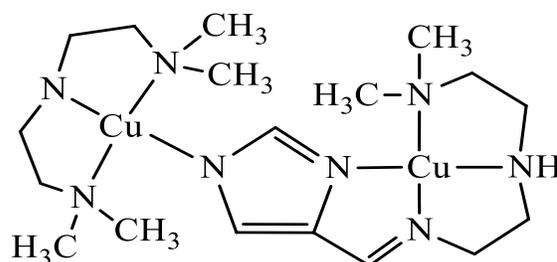
Representative examples of first method are Cu(II) complexes with multidentate Schiff-base ligands containing imidazole groups. These Schiff base ligands have both donor and acceptor abilities in the formation of coordination bonding. Under the acidic condition condensation of 4-formylimidazole and *N,N*-dimethyldiethylenetriamine form compound **1** as shown in (**Figure 16**). Compound **1** reacts with itself in the presence of the base to give imidazolite bridge species **2** (**Figure 17**). Here the compound **1** acts as metal organic ligand and react itself to form the homodinuclear complex [48]. Improvement in the work was done by isolation of a mono-deprotonated species **3** which is the mononuclear complex with the free amine of the ring skeleton by Brewer and coworkers [49]. This complex functions as monodentate ligand complex i.e. metal complex as ligand and reacts with the other mononuclear complex, tetraphenylporphyrinato Fe(III) to give linear trinuclear complex **4**.

The same concept was used to synthesize the trinuclear complex (**Figure 18**). The mononuclear complex of Cu(II) ion of unsymmetrical tetradentate ligands containing an imidazole group per molecules were synthesized [50]. The mononuclear complex of Cu(II) was self – assembled to the mononuclear complex of iron to form various polynuclear complexes such as compound **5** (**Figure 19**). Here, Y. Sunatsuki has used precursor complexes which act as MOLs and form a variety of the heteropolynuclear complexes with metal variants [51].



1

Figure 16 Mononuclear MOL



2

Figure 17 Homodinuclear complex from MOLs

The new concept of reacting the coordinated amine with the free aldehyde group of the mononuclear complex to form trinuclear complexes by the Schiff base reaction with two mononuclear complexes was reported by S. Deepalatha and coworkers. The copper(II) complex of 3,4-dihydroxy benzaldehyde as the ligand system in which the aldehyde group could be modified to attach additional nitrogen donor sites through Schiff base condensation has been attempted. The formation of trinuclear complexes using the two kinds of metal complexes with reactive sites [9]. In first step 2,2'-bipyridyl 3,4-dihydroxy benzaldehyde monometallic cupric(II) complex was allowed to react with

diethylenetriamine complexes of Cu(II), Zn(II) and Ni(II) to produce trinuclear complexes (**Figure 20**). The template synthesis of the trinuclear complexes in which, the coordinated amine undergoes Schiff base reaction with free aldehyde group of precursor complexes.

The coordinated aldehyde and amine undergoes the Schiff base reaction and form the new homo and hetero dinuclear complexes by inter complex reactions reported by V. D. Bhatt and Samat Ram. Here, the mononuclear complexes acts as MOLs and undergo the Schiff base reactions (**Figure 21**). The mononuclear complexes of *o*-aminophenol with salicylaldehyde and *o*-vaniline were formed with different metal ions [17, 52, 53].

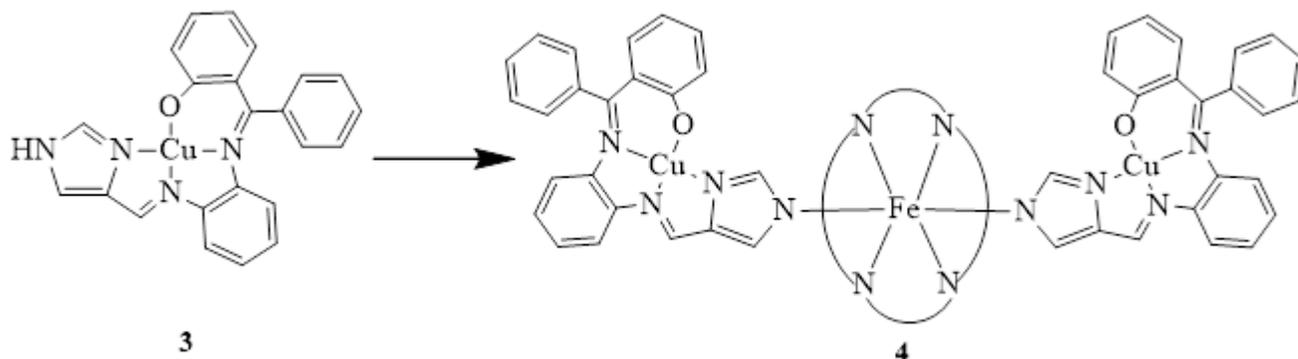


Figure 18 Heterotrimeric complex from mononuclear MOLs

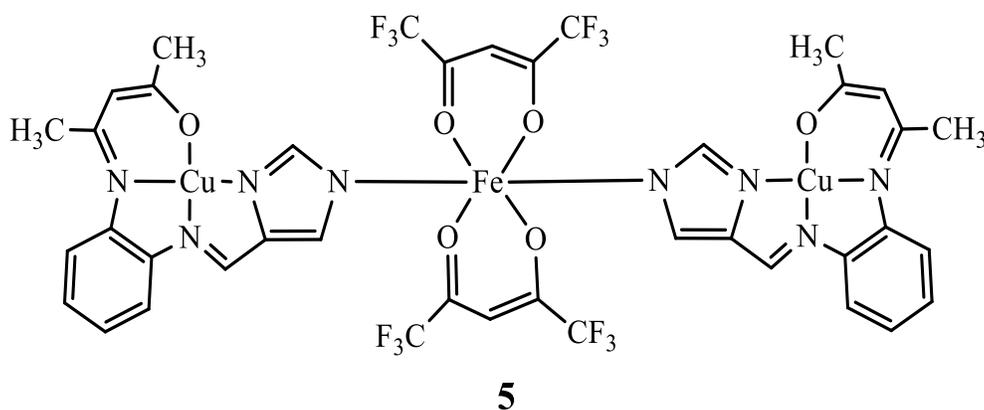


Figure 19 Heterotrimeric complex

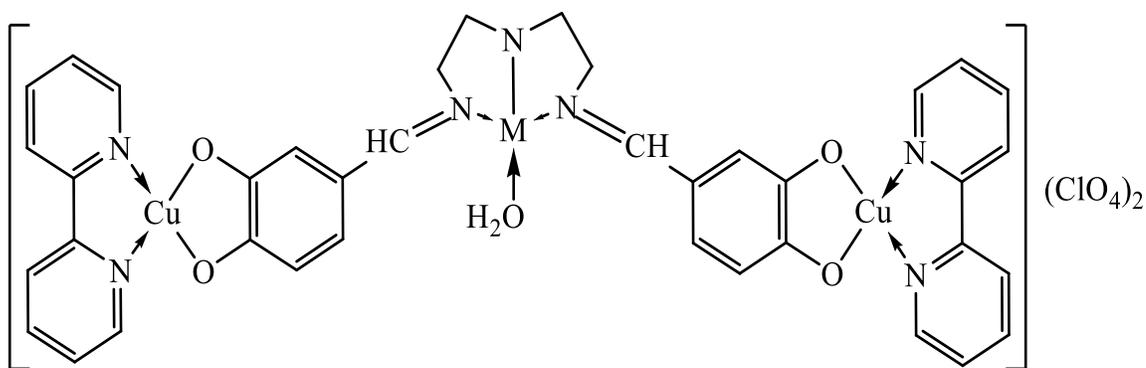


Figure 20 Heterotrimeric complex

Application of polynuclear complexes

The transition metal complexes are widely used in catalysis but dinuclear Schiff base complexes of transition metal ions are more efficient catalysts than mononuclear complexes probably due to the synergistic effect of two metal ions. The metal complexes exhibit a lot of bioactivity such as antimicrobial activity, antiviral activity, antifungal activity, analgesics, HIV protease and anticonvulsants [1, 2]. The polynuclear complexes generally exhibit interesting magnetic properties, moreover magnetic properties of materials have been utilized over years in mechanical applications such as electric motors, electric generators as well as in communication technologies such as television and telephones. More recently, magnetism has found extensive application in the area of data storage and processing, from magnetic tape to floppy discs and computer hard drives [13]. Traditional magnetic materials consist of two- and three-dimensional structures of transition metal or lanthanide metal containing spin units. In contrast to that, molecular magnets are organic or inorganic/organic hybrid materials consisting of either metal with spin units or organic radical containing spin units. Such molecular magnetic materials can possess better optical properties and the combination of magnetic properties with other properties like mechanical, electrical and / or optical properties makes them easily processable [33, 34]. In the last two decades, an increasing interest in polynuclear complexes containing ligand structures capable of holding two or more metal centers in close proximity to act as single molecular magnets has been observed. The field of molecular magnetism exhibited a rapid development in the last two decades with a particular emphasis on heteropolymetallic complexes.

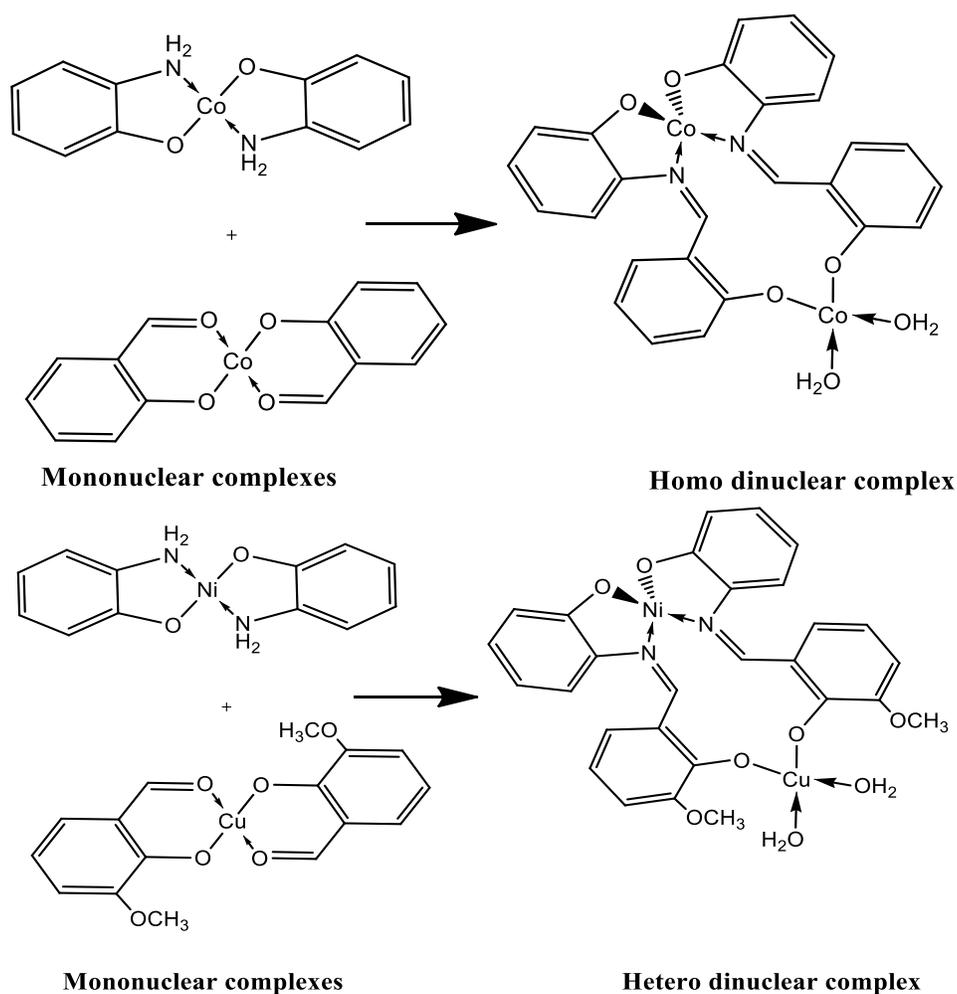


Figure 21 Homo and heterodinuclear complexes.

Concluding remarks

The different types of ligands, which are the electron rich compounds, play varying important roles in coordination chemistry. Attempts to synthesize polynuclear complexes of specific structure by one pot method using simple anion ligands give rise to the formation of mixtures of different types of metal complexes, whereas the use of polytopic ligands and metal organic ligands (MOLs) are more efficient for the preparation of such polynuclear complexes. Amongst the various methodologies for the synthesis of tailor made polynuclear complexes with expected structures, using "metal complexes as ligands" is the most successful, especially for heteropolymetallic complexes. The mixed ligands complexes and its studies documented well but, now researches takes more interest in mixed metal complexes with higher nuclearity. The polynuclear complexes exhibits the variety of chemical and physical properties with variation of metal ions. An achievement of single crystal of polynuclear complexes is the big challenge for inorganic chemists and the self-assemble method is more useful.

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