



## POLYNUCLEAR HETEROMETALLIC COMPLEXES DERIVED FROM "SALEN" TYPE $N_2O_4$ DONOR DI-SCHIFF BASE LIGANDS

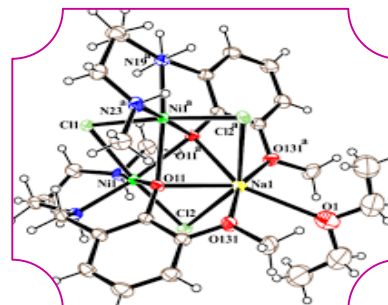
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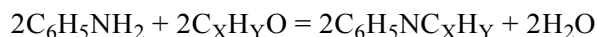
### ABSTRACT

This paper contains a comprehensive review on polynuclear heterometallic complexes derived from "salen" type  $N_2O_4$  donor di-Schiff base ligands. "salen" type di-Schiff base is 1:2 condensation products of ethylenediamine (or its derivatives) and salicylaldehyde (or its derivatives). Synthesis, nuclearity, structure and magnetic properties of complexes are elaborately explained.

**KEYWORDS:** Schiff base, Polynuclear, Heterometallic, Polynuclear, Crystal Structure, metalloligands.

### INTRODUCTION:

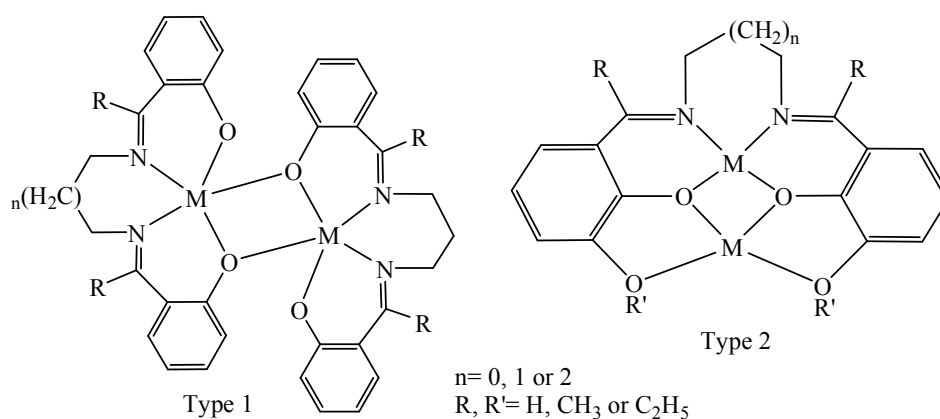
In the year 1864, Hugo Schiff first synthesized the Schiff bases by the condensation of aniline with aldehydes including acetaldehyde, benzaldehyde and cinnamaldehyde and he discovered that imines were formed (Scheme 1). The first brief paper was entitled "A New Series of Organic Bases"[1]. Since then various types of Schiff bases have been synthesized; all are not the singly condensed Schiff bases but also are di- or even tri-condensed ones [2].



**Scheme 1.** Reaction of aniline with carbonyl compounds

In the year 1923, Middleton *et. al.* first reported the use of Schiff bases as ligands for binding metal ions [3]. After that, several coordination chemists have built a large number of metal complexes with the Schiff base ligands. Numerous types of Schiff bases have been used for this purpose and initially only the imino nitrogen atoms of the Schiff bases were considered as donor centers. Later, various substitutions were introduced in both the carbonyl and amine fragments so that they had additional donor atoms to be coordinated to the metal ion *i.e.* the Schiff bases became polydentate chelating ligands. Even at present, arguably one of the most popular chelating ligands are the salen type di-Schiff bases, the 1:2 condensation products of ethylenediamine (or its derivatives) and salicylaldehyde (or its derivatives). The popularity of this salen type Schiff bases stems from the fact that they can be synthesized very easily and the two imine nitrogen atoms as well as the two phenoxido oxygen atoms can coordinate to a metal centre making them very useful tetradentate chelating ligands. The complexes of several metals ions, mostly of the transition metals *e.g.* Zn(II), Cu(II), Ni(II), Co(II/III), Fe(II/III), Mn(II/III), Cr(III), V(IV/V), Cd(II), Hg(II) have been reported. The complexes have been characterized by various techniques and before 1960s; the spectroscopic

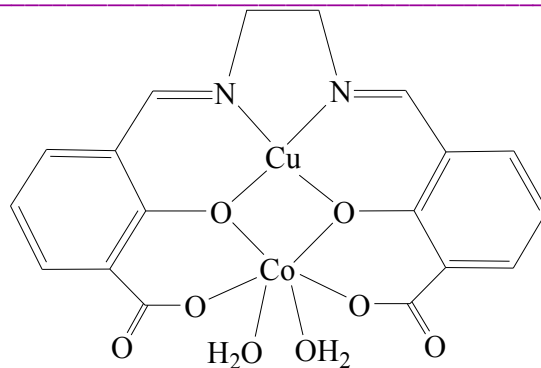
techniques such as NMR, PMR and EPR along with elemental analyses were used to propose the structure as well as the nuclearity of the derived complexes. In 1960, structure of a Schiff base bound metal complex was first determined by X-ray crystallography [4]. Since then single crystal X-ray analysis became an essential tool for the characterization of such complexes. It has been found that most of the complexes, especially with the divalent metal ion, where the tetradentate di-negative ligand satisfies both the charge and four coordination numbers of the metal ions are mononuclear with square planar geometry. However, the solvent molecules can also coordinate to one or both the axial positions to make the geometry of the mononuclear complexes square pyramidal or octahedral, respectively. In many cases, the coordinated phenoxido oxygen atoms bind additionally to the axial position of a neighboring molecule to form dinuclear complexes. The dinuclear complexes can also be formed very conveniently by using suitable substitution in the phenyl ring of salicylaldehyde. For example, a methoxy/ ethoxy/ carboxylato group in the other *ortho* position of the phenolic -OH creates two compartments with  $N_2O_4$  donor sites to accommodate two metal ions with the help of bridging phenoxido oxygen (Scheme 2).



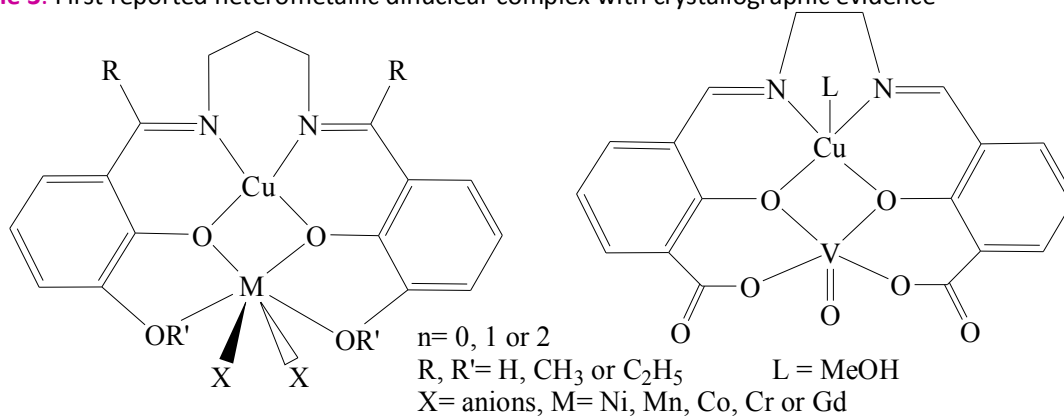
**Scheme 2.** Two different types of dinuclear complexes

### Heterometallic dinuclear and trinuclear complexes with $N_2O_4$ donor di-Schiff base ligands

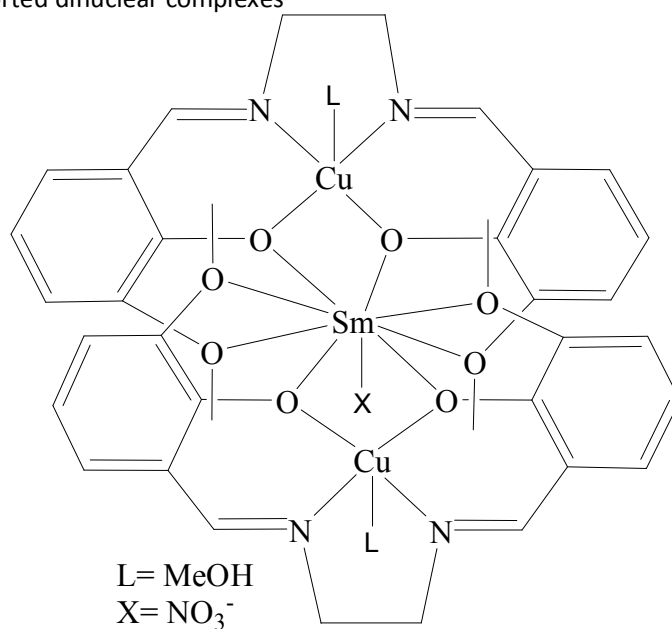
The heterometallic polynuclear complexes have generally been synthesized with the help of two main approaches. The first one is based on a very simple idea: metal ions show different affinity towards different coordinating atoms and thus, the combination of ligands bearing different donor atoms with a mixture of metal ions is expected to lead to the self-assembly of well-ordered heterometallic systems [5]. The second strategy (Sinn *et. al.* reported [6] in 1969) consists of using previously formed metal complexes having vacant coordination sites with potentially bridging group or labile ligands. These complexes can act as ligands and coordinate to additional metal centers. This “complex as a ligand” approach has been applied successfully by several groups to construct many polynuclear complexes especially heterometallic complexes [7]. In the last few decades, this approach has been preferred over the other strategies because getting the target molecule is much easier especially when the “metalloligands” have reasonable solubility in the common organic solvents. In 1978, Okawa *et. al.* synthesized a heterometallic dinuclear Cu-Co complex and characterized it by X-ray crystallography (Scheme 3) [8]. Later several groups synthesized quite a few dinuclear heterometallic complexes (Scheme 4) using this strategy [9]. In recent years, various groups especially Costes *et. al.* [10] and Andruh *et. al.* [11] have been expanding this field of heterometallic complexes by utilizing various “metalloligands”. Using the same strategy, they also synthesized few trinuclear complexes [12] in which a second metal atom is trapped between two metalloligands (Scheme 5). The increase of the nuclearity from two to three influenced the magnetic properties significantly because three paramagnetic centers interact through phenoxido and/or other short bridges showing extraordinary results.



**Scheme 3.** First reported heterometallic dinuclear complex with crystallographic evidence



**Scheme 4.** Various reported dinuclear complexes

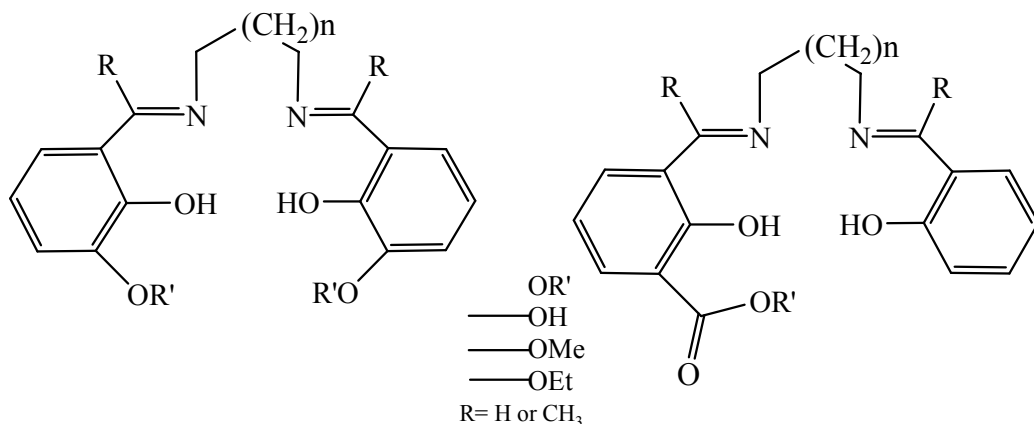


**Scheme 5.** Reported trinuclear complex by Andruh *et. Al*

#### Heterometallic polynuclear complexes with $\text{N}_2\text{O}_4$ donor di-Schiff base ligands

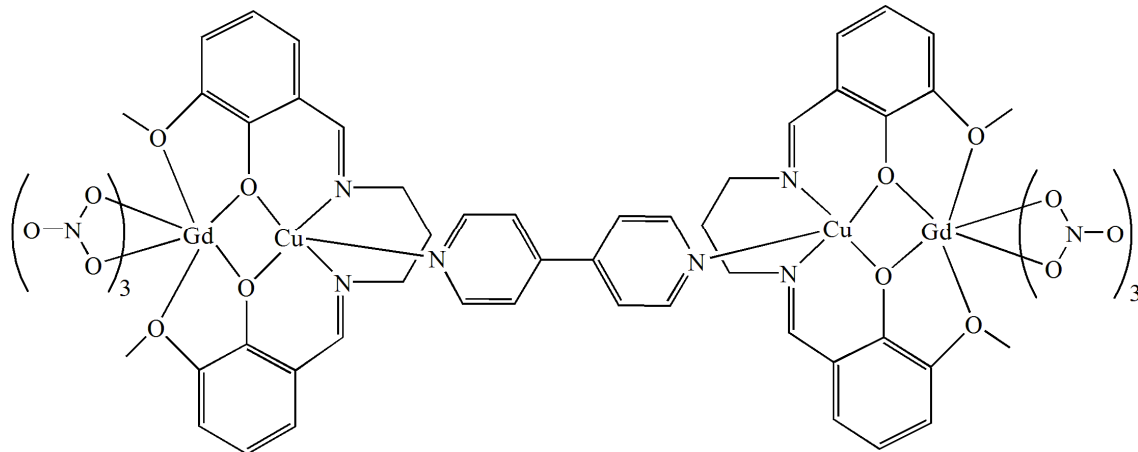
As mentioned in the preceding paragraph, the  $\text{N}_2\text{O}_4$  donor di-Schiff base ligands are very useful to obtain heterometallic complexes because it has two separate compartments with different coordinating

environment which can accommodate two different metal ions according to their preference for coordinating atoms (Scheme 6).

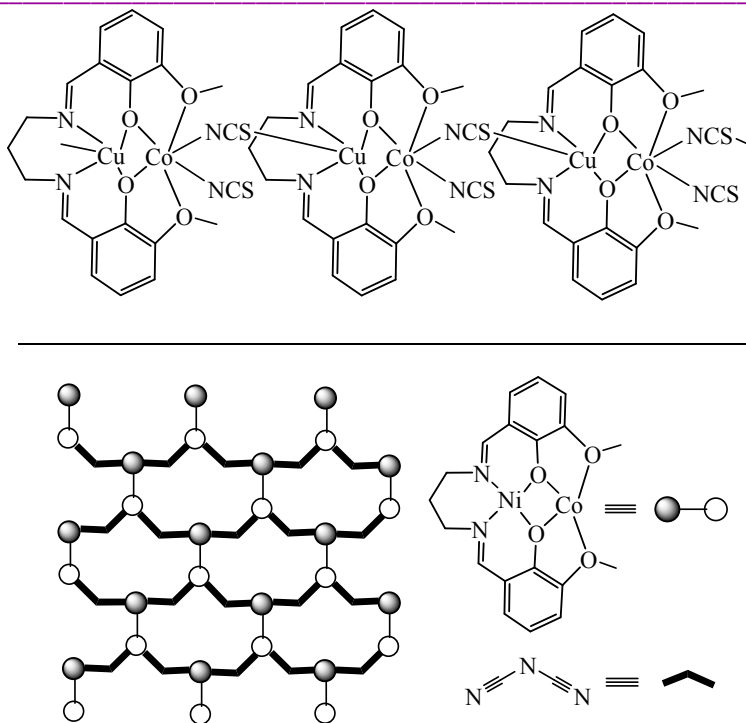


**Scheme 6.** Common  $\text{N}_2\text{O}_4$  donor di-Schiff base ligands with two separate compartments

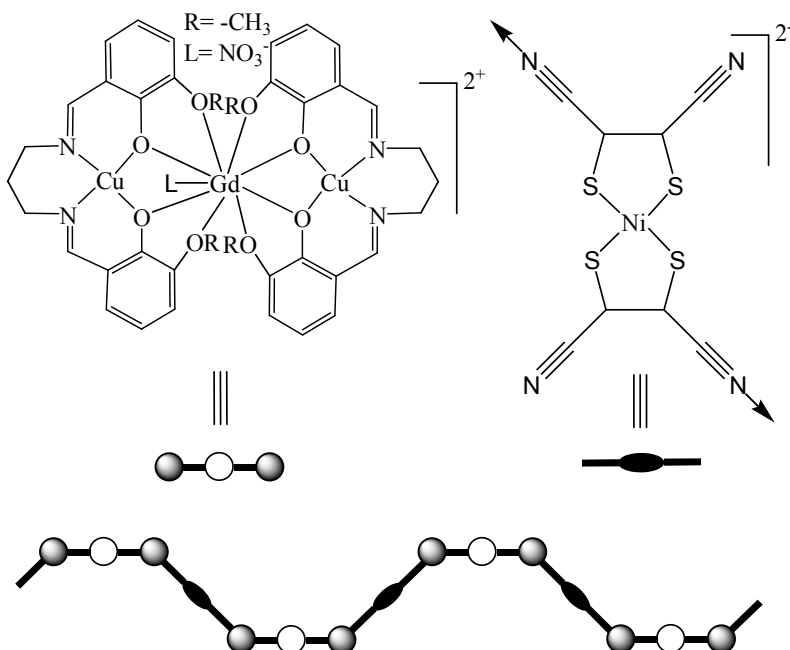
In a quest to increase the nuclearity of such complexes, Andruh *et. al.* first used these dinuclear heterometallic complexes as nodes and joined them with the help of spacers like isonicotinate, 4,4'-bipyridine, dicyanamide, dicarboxylic acid *etc.*, a technique first proposed by Robson *et. al.* [13]. Using these techniques, five tetranuclear [14] (Scheme 7) and a lot of polynuclear complexes [11a, 15] have been synthesized. The schematic representation of 1D and 2D polymeric complexes are shown in scheme 8. The trinuclear heterometallic complexes have also been used as nodes by Andruh *et. al.* for the synthesis of few interesting coordination polymers [11a, 15] (Scheme 9) or discrete [11] polynuclear complexes (Scheme 10).



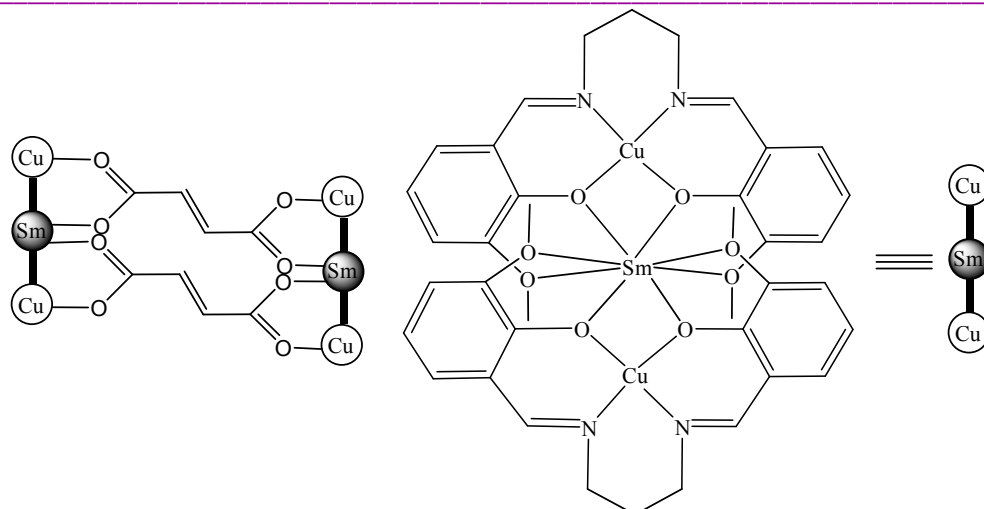
**Scheme 7.** Formation of a tetranuclear complex from two dinuclear nodes



**Scheme 8.** 1D (upper) and 2D (lower) polymeric complexes build by dinuclear nodes

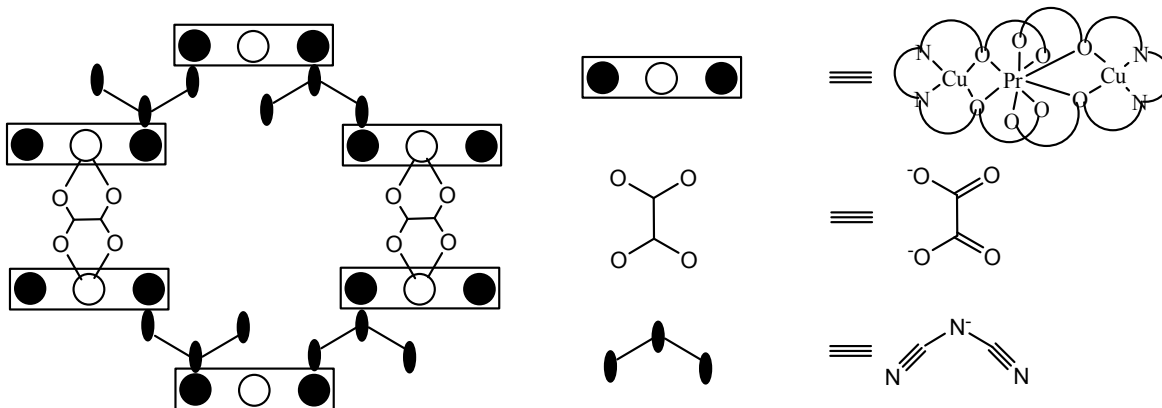


**Scheme 9.** 1D polymeric complex build by trinuclear nodes

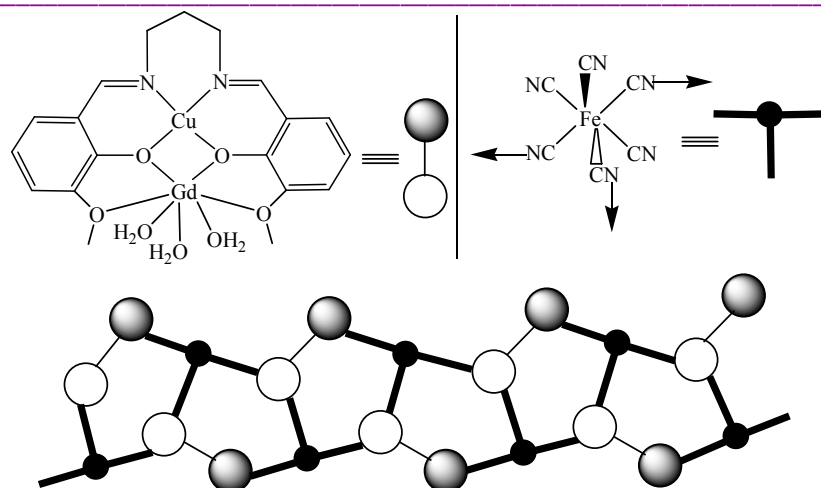


**Scheme 10.** Formation of a hexanuclear complex by trinuclear node

These types of  $N_2O_4$  donor ligands have also been utilized to synthesize cyclic heterometallic complexes [11a] (Scheme 11,  $\{(CuL''')_2Pr\}^{3+}$  node where  $L''' = N,N'$ -propylenedi(3-methoxy salicylideneiminato)). A few of them are constituted by three different metal containing trimetallic units [16] (Scheme 12). These complexes can show interesting magnetic properties which arise from the interactions of three different spins [17]. Moreover such three different metal containing compounds can be multifunctional [18]. For example, two hetero metal may give magnetic coupling and the third one can have luminescent properties [19]. These trinuclear nodes have been used to form porous 3D polymer with long bridging spacers that showed interesting gas absorption properties [20].



**Scheme 11.** Cyclic heterometallic complex built by trinuclear nodes



**Scheme 12.** Cyclic heterometallic complex built by three different metal ions

### CONCLUSION:

Almost a century and a half later after the invention of Schiff bases, till this date, Schiff bases are being used in large numbers in the field of coordination chemistry. Among all the Schiff base ligands, tetradentate di-Schiff ligands are most commonly used and are very popular for its binding ability towards various metal ions. However, as discussed in the preceding sections, although the bridging ability of a “metalloligand” towards second metal atoms is known and exploiting this property some heterometallic complexes have been prepared but a systematic study on the nuclearity and shape of the complexes has not been done. For example, one two or three metalloligands can coordinate to the second metal ion to form di-, tri- and tetranuclear complexes respectively. Formation of such complexes may depend upon various factors *e.g.* nature of the Schiff base used, preferred coordination environment of the second metal ion, binding ability of the anionic coligands, solvents for the synthesis *etc.* Atakol *et. al.*, used coordinating solvent (*e.g.* DMF, DMSO, dioxane *etc.*) for the synthesis, coordination of which to the metal ions may hamper the formation of the higher nuclear complexes. Therefore, we decided to use less coordinating solvents *e.g.* methanol, acetonitrile, ethanol *etc.* for synthesis. We would like to investigate how the coordinating ability of the bridging anionic ligands influences the nuclearity and molecular shape of the resulted heteronuclear complexes.

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