REVIEW

Metal-Ligand Coordination Driven Di/Tri-nuclear Helicate and Mesocate: A Brief Review

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Helicity is a geometric motif that can be observed in nature as well as artificial structures. In synthetic supramolecular architectures, helicity can be incorporated by conformational restrictions of macromolecules, inter- or intra- molecular hydrogen bonds or coordination to metal ions. In present brief review, the discussions will be restricted on the metal-ligand coordination driven self-assembled di/tri-nuclear helical structures. Furthermore, the chirality of the helical structures is enlightened, which arises due to preferential orientation of the ligand strands around the metal centers that comprise the formation of two type helicates, one is homo-chiral helicate and the other is hetero-chiral helicate or mesocate.

Keywords: Self-assembly, Helicate, Mesocate, Homo-chiral, Hetero-chiral.

INTRODUCTION

Metal ion mediated self-assembled helical compounds are one of the most important and remains a crucial area for research over the last three decades [1-4] because of their involvement in new areas of research such as anion sensors [5,6], chirality, luminescence, magnetism, molecular machines [7], guest recognition and DNA binding [8]. In contrast, achiral meso-helical structures had shown great potential towards molecular wires and molecular switches, information storage and processing nanotechnology [9]. Lehn [1] introduced the term "helicate" for metal complexes that contain one or more ligand strands and two or more metal centers [1]. After 10 years, in year 1997, Piguet *et al.* [2] brought the helicates into the limelight through a review article on the basis of number of ligand strands and metal ions present in their architectures [2]. Since then, several articles have been published on helicate compounds based on diverse ligand strand, varied metal ions and their emerging applications [3,10-16]. The present short review primarily discusses the classification of di-nuclear and tri-nuclear helicates based on their double-stranded and triple-stranded structures. The classification is determined by the chirality of the helicates, which can be either homo-chiral or hetero-chiral. Representative examples are included to exemplify the varieties of helicates.

Principle of helicate construction: The challenge of helicate chemistry is to understand fundamental principles of self-assembly processes. Fig. 1 describes the principles of helicate construction. The line connecting two or more metal ions defines the helical axis in metal-ligand coordination helical complexes and the ligands create the strands of the helix by complexing with the metal ions and twisting around the axis. The three basic elements of the structure are the metal ion, the chelating binding site on the ligand and the bridging unit that joins binding sites, coordinating different metal ions. In general, the metal ions have more or less strongly preferred coordination geometry, defined by a coordination number and a geometrical disposition such as tetrahedral for Cu^+/Ag^+, octahedral for $Fe^{2+}/Co^{2+}/Ni^{2+}$, coordination number of 8 or 9 for the larger lanthanides and so on. The first element of structural control is the coordination preference of the metal ions. The binding site of the ligand is the second element and is defined by its denticity, *i.e.* the number of atoms that bind to the metal: 2 (bidentate) for bipyridines or catechols, 3 (tridentate) for terpyridines, *etc.* To satisfy its coordination preference of the metal ions, the total number of atoms that bound to the metal is an important criterion towards the formation of helicates. In case of a tetrahedral ion such as Cu^+, two bidentate sites will participate to
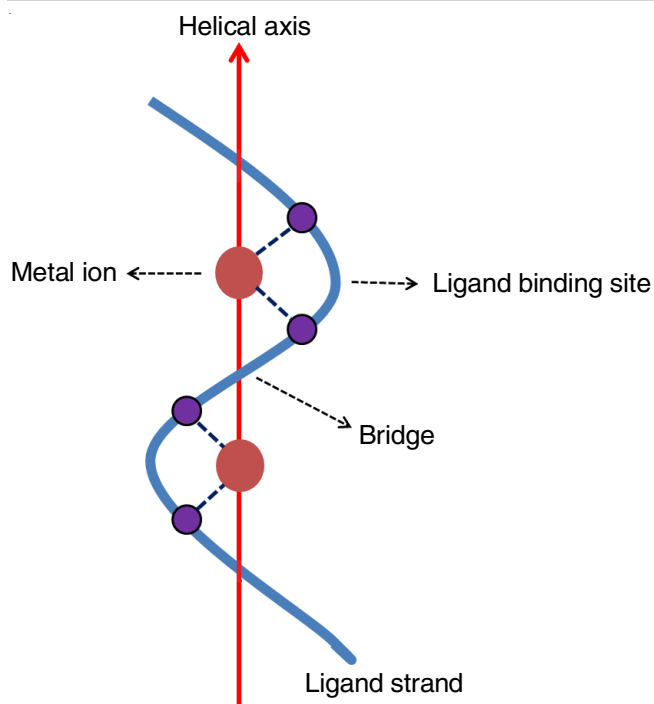
Fig. 1   Different structural elements of helical complexes. Only one ligand strand is shown

(a) Homo-chiral either ΔΔ or ΛΛ chirality at the metal centers

(b) Hetero-chiral either ΔΛ or ΛΔ chirality at the metal centers

Fig. 2.   Pictorial representation of Homo-chiral (a) and Hetero-chiral (b) Hetero-chiral either ΔΛ or ΛΔ chirality at the metal centers

form a double stranded helical structure [17]. However, for octahedral metal centre three bidentate sites or two tridentate sites are required for the formation of a triple helix [18] or a double helix, respectively. Similarly, the higher coordination numbers of lanthanide complexes may be satisfied by three tridentate sites for triple helix formation *via* nine coordination of the metal centre [19]. Moreover, the bridging unit of the ligand strands that connect the chelating groups is crucial towards helical structure formation. In general, bridging unit should be flexible enough to allow the ligand to wrap around the helical axis, but sufficiently rigid to prevent the second binding site from twisting round to coordinate the first metal and to ensure that the helical chirality of one metal is transmitted to its neighbour. These three structural elements given above may be varied by the synthetic designs to control the desired helical structure formation.

Chirality of helicates: In coordination chemistry, the concept of helicity originates nearly as far back as the development of coordination theory by Alfred Werner. The 1,2-diaminoethane(en) ligands in $[Co(en)_3]^{3+}$ could twist either clockwise (Δ) or anticlockwise (Λ) around the C_3 symmetry axis of the complex [20]. Therefore, the chirality of the helicates arises due to helical wrapping of the ligand strand around the metal centres. Di-nuclear helicates can be divided into two types according to the chirality at the metal centres. One, is homo-chiral *i.e.* either Δ or Λ configuration in both the metal centres [21-23] as shown in Fig. 2a. Besides homo-chiral helicates, there are hetero-chiral (Δ and Λ) helicates with alternating Δ and Λ configuration are also possible (Fig. 2b) [24-27]. This types of arrangements at the coordination sites with a mirror plane at the centre of the helicate, makes the overall helicates as a whole an achiral meso-forms and is known as meso-helicates
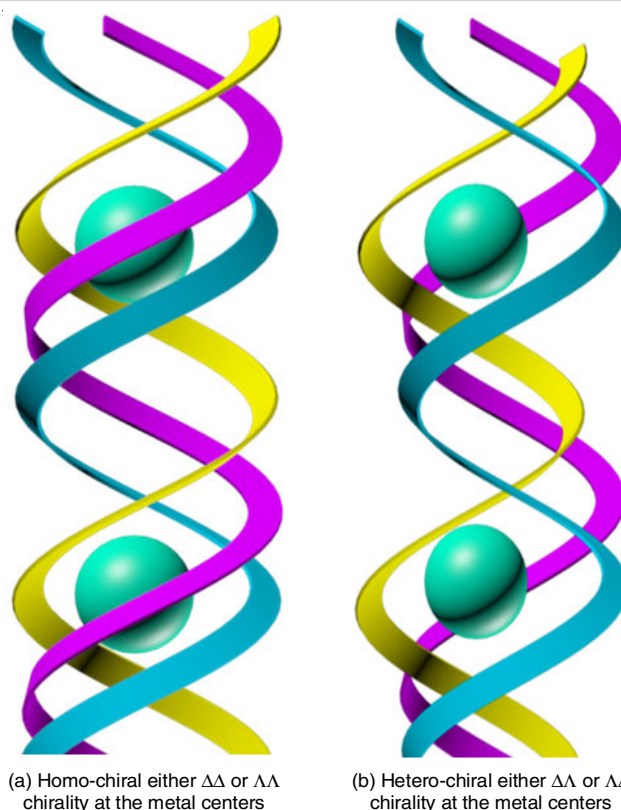
or mesocates. Therefore, a judicious choice of bridging ligands and the metal ions is crucial for deliberate formation of halicate structures with the ligands twisted around the metal ions, which are located in homochiral environments (Δ or Λ). In contrast, a side-by-side binding of the ligands around the metal centres offered mesocate achiral structures with the metal ions exhibiting opposite chirality (Δ and Λ).

If one extends the di-nuclear helicates into tri-nuclear one by adding another metal centre, two types helicates may formed. One is homo-chiral helicates (ΔΔΔ or ΛΛΛ) that arises due to extension of helical wrapping of the ligand strand along the helical axis [28]. On the other hand, di-nuclear mesocates transformed into tri-nuclear helicates with an additional metal centre, in which the metal centres possess alternating Δ and Λ chirality (ΔΛΔ or ΛΔΛ) [29-31]. The odd number of metal centres makes them chiral overall and the ligands do not wind around the helix, but rather bind in a parallel zig-zag fashion. These complexes are called side-by-side helicates [32]. However, when the ligand strand does not possess any chiral centers, most of the homo-chiral helicates are obtained as recemic mixture of two chiral enantiomers of homo-charal helicates (*i.e.* 1:1 mixture of ΔΔ and ΛΛ in case of di-nuclear helicates). Still, it is possible to obtain only one of the helical isomers by spontaneous separation during crystallization [33]. On the other hand, it is possible to came up with a particular chiral helicates (ΔΔ or ΛΛ) by introducing a chiral substituents at the ligand [23].

Historical background of helicates: It is reasonable to relate the beginning of current interest in helical complexes

with a paper by Lehn in 1987, in which the oligo-bidentate ligands **1** and **2** have shown to form double stranded homo-chiral helical complexes with two and three Cu⁺ ions, respectively (Fig. 3) [17]. Prior to 1987, few helical complexes are reported in the literature; yet, these helical structural motifs had not been discussed [34]. Similar to the terminology used for cryptands and cryptates, [35] corresponding ligands were referred to as "helicands" and their complexes as "helicates". Since 1987, a large number of helicates with different nuclearity, metal ions and ligand strand along with their interesting properties have been reported in the literature.

Di-nuclear M₂L₂ helicates: After introduction of di-nuclear [Cu₂**1**₂]²⁺ helicates, Lehn further introduced ligand **3** close to the system **1** where the flexibility of the spacer is reduced

(Fig. 4). The ether linkage -CH₂-O-CH₂- of ligand in **1** was substituted by an imine-unit, -CH=N-CH₂- in case of **3**. The ligand **3** upon complexation with Cu⁺ and Ag⁺ ions form di-nuclear double stranded helicates [Cu₂**3**₂]²⁺ and [Ag₂**3**₂]²⁺ [36]. In recent times, Fabbrizzi *et al.* [37] demonstrated another Cu⁺ template M₂L₂-helicate with a *bis*-bidentate ligand (**4**) which is obtained by Schiff base condensation of *RR*-1,2-cyclo-hexanediamine and 8-naphthylmethoxyquinoline-2-carbal-dehyde (Fig. 4). The *bis*-bidentate ligand **4** reacts with Cu⁺ to form a stable helicate complex, [Cu₂**4**₂]²⁺, whose strands are held together by eight Cu–N coordinative bonds and by four additional π–π intra-complex interactions, involving a quinoline sub-unit of one strand and a naphthylmethoxy substituent of the other strand. This conveys an extra high stability to the
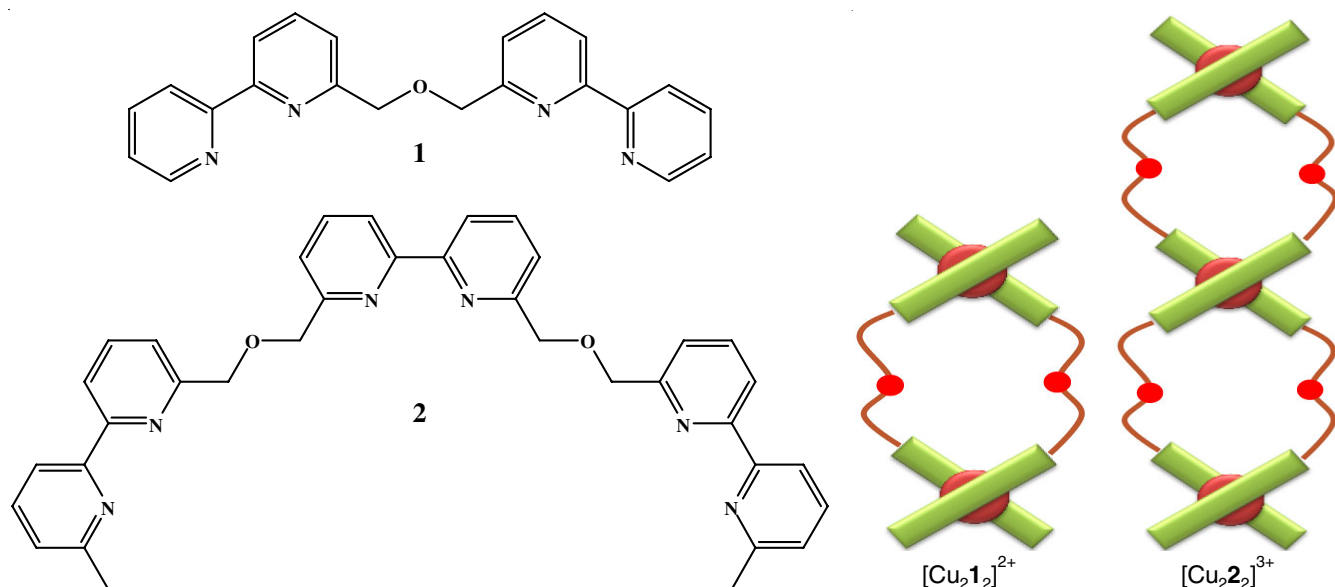

Fig. 3. Pictorial representations of dinuclear double stranded helicate [Cu₂**1**₂]²⁺ (left) with ligand **1** and trinuclear double stranded helicate [Cu₃**2**₂]³⁺ (right) with ligand **2**
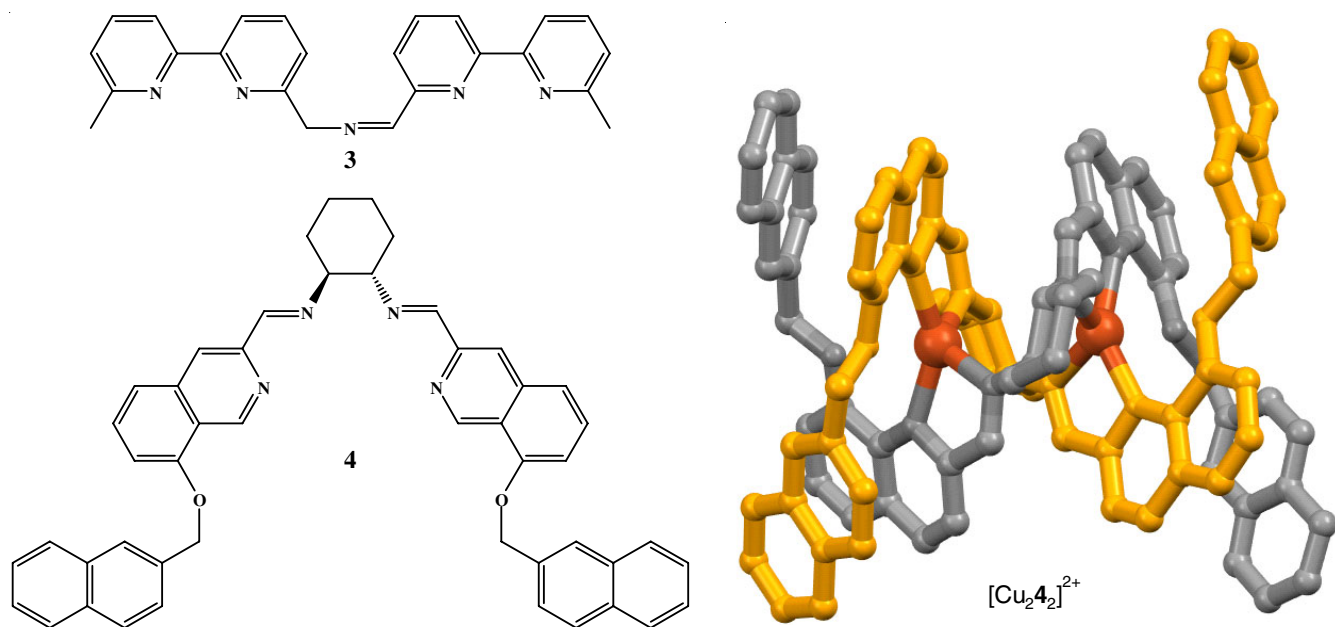

Fig. 4. Representation of ligands **3**-**4** and single crystal X-ray structure of dinuclear double stranded helicate [Cu₂**4**₂]²⁺ with ligand **4**

helicate complex, which does not decompose on addition of an excess of either the helicand **4** or Cu+ ion.

Di-nuclear M₂L₃ helicates: Moreover, since 1970s, di-nuclear triple-stranded helical coordination complexes have been reported. A naturally occurring siderophore called rhodo-turulic acid (**5**-H₂) was isolated from low iron cultures of rhodotorulapilimanae and related yeast (Fig. 5) [38]. This siderophore is important for the control of the iron uptake in microorganisms [39]. Rhodoturulic acid formed di-nuclear complexes with Fe^{3+}, Cr^{3+} and Al^{3+} ions, as reported by Raymond & Carrano [40]. Circular dichroism (CD) experiments demonstrated that both complex units of di-nuclear triple-stranded helicates [M₂**5**₃] (M = Fe, Cr and Al) have the same configuration Δ. The compounds are hence triplestranded (P)-helicates. The only helicate discovered in nature prior to 1985 was the di-iron complex of rhodoturulic acid [Fe₂**5**₃] [40]. Raymond presented the **6**-H₂ derivative of *bis*(hydroxypyridinone) as an artificial analogue of rhodo-turulic acid (Fig. 5). Two hydroxamic acid binding sites are present in both ligands for the purpose of coordinating metal ions. Fe^{3+} and **6**-H₂ combine to produce a triple-stranded di-nuclear complex [Fe₂**6**₃], which takes on a helical shape in the solid state and contains a single water molecule inside of it [41]. In 2012, Dolphin [42] demonstrated the impact of substituents in the bridging unit of ligand strand towards the formation of helicates by adopting ligand **7**-H₂, which lacks a substituent in the methylene bridge and ligand **8**-H₂, which has a *gem*-dimethyl substitution.

Ligand **8**-H₂ has shown predominant formation of di-nuclear triple stranded [M₂**8**₃] helicates over mesocates with different trivalent metal ions such as Fe^{3+}, Co^{3+}, Mn^{3+}, Ga^{3+} and In^{3+}. This finding suggests that the degree of substitution on the linker carbon, in addition to the length, position and rigidity of a linker, has a significant impact on the supramolecular self-assembly of these systems. It is therefore necessary to take into account each of these factors when designing similar ligands in the future in order to influence the stereoselectivity of the self-assembly. Hooley *et al*. [43] presented a *bis*-tridentate ligand **9**-H₄, that forms self-assembled M₂L₃ helicates with the lanthanide ions with a kinetic preference for smaller metal ions and a thermodynamic preference for larger metal ions. Selectivity is found despite small differences in size of the Ln ions and identical coordination environment of the ligand.

Di-nuclear M₂L₂/M₂L₃ mesocates: The term meso-helicate or mesocate was first used in 1995 by Albrecht & Kotila [44] to describe a unique kind of di-nuclear triple stranded achiral helical complex of a *bis*-catechol ligand (**10**-H₄), which is separated by three methylene spacers (Fig. 6). It reacts with Ti^{4+} to form di-nuclear triple stranded mesocate [Ti₂**10**₃]⁴⁺, where the metal centres possess opposite chirality (Δ and Λ). Since the discovery of first synthetic mesocate by Albrecht in 1995, different polytopic ligands have been used for the synthesis of mesocates to explore their various interesting properties. In 2011, Pedrido *et al*. [45] successfully obtained a new type of extended supramolecular 2D array, the 'grid-of-mesocates', by using *bis*-thiosemicarbazone ligand (**11**-H₂) and applying the 'sequential self-organization strategy' (Fig. 6). Further, Pardo *et al*. [46] have shown the formation of two metallocyclic mesocates Na₈[M₂L₃], M = Ni^{2+} and Co^{2+} in aqueous solution

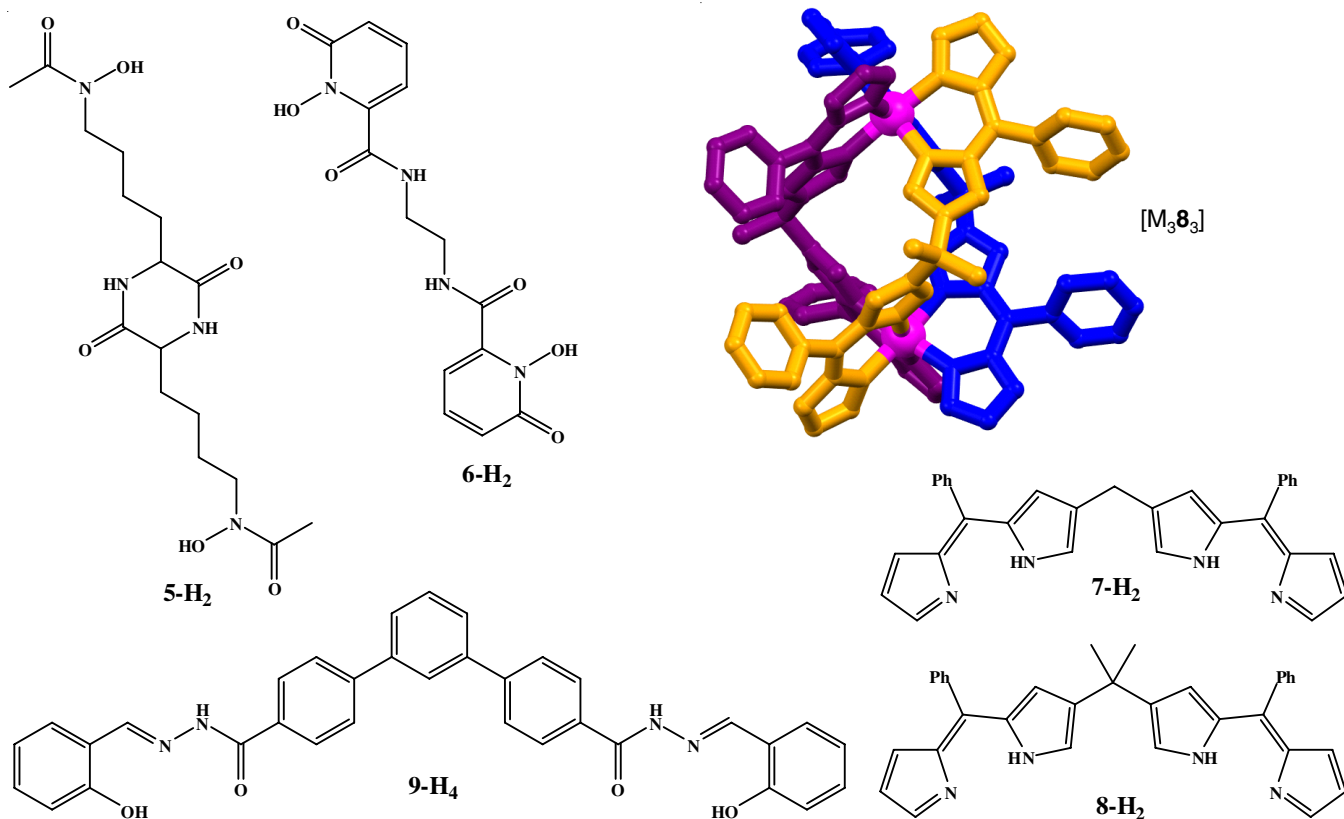Fig. 5. Representation of ligands **5-9** and single crystal X-ray structure of dinuclear triple stranded helicate [Ga₂**8**₃] with ligand **8**

$[Co_2 11_2]$

$[Ni_2 12_3]^{8-}$
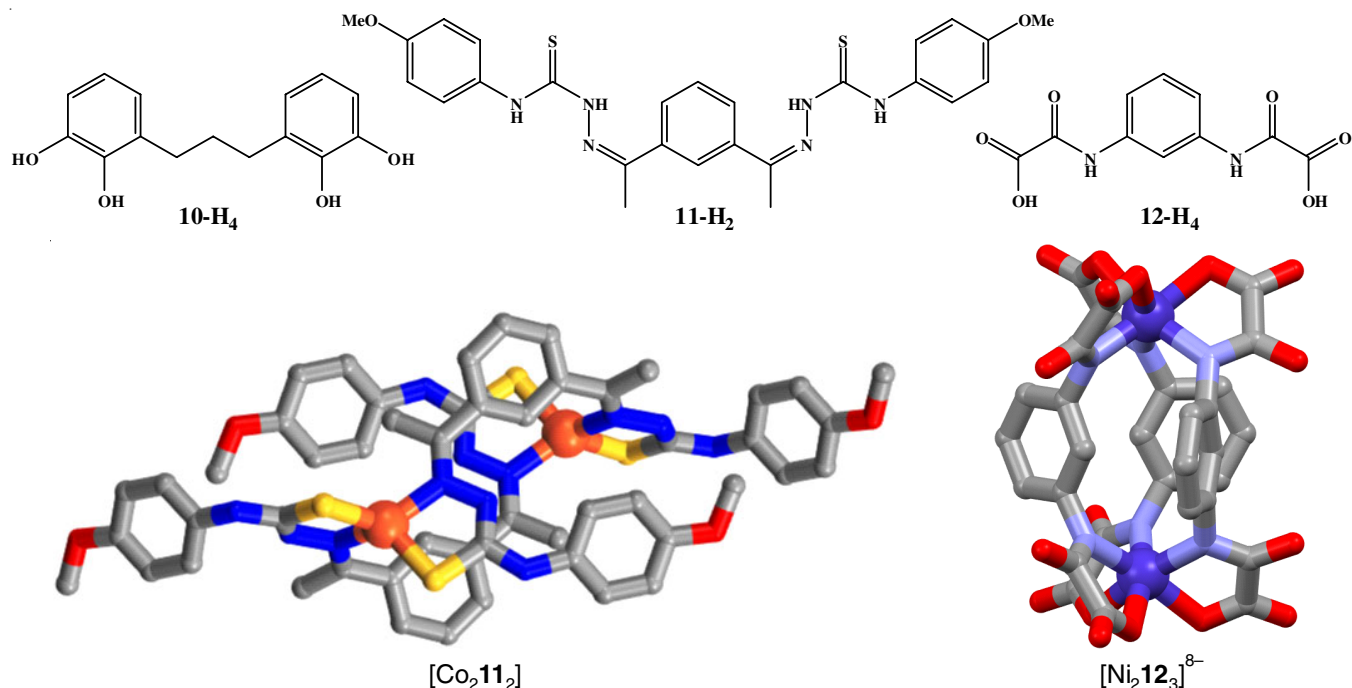
Fig. 6. Representation of ligands **10**-**12** and single crystal X-ray structure of dinuclear double stranded helicate $[Co_2 11_2]$ with ligand **11** and dinucleartriple stranded helicate $[Ni_2 12_3]^{8-}$ with ligand **12**

from a *N,N′*-1,3-phenylene*bis*(oxamicacid), (**12**-H$_4$) (Fig. 6). The triple stranded meso-helicate molecular structure is promoted by the relatively short and rigid feature of the phenylene spacer that prohibits helical twisting around the metal centres to generate the more typical helicates. The ability of aromatic *meta*-substituted phenylene spacers to transmit ferromagnetic electron exchange interactions between paramagnetic metal centers separated by comparatively long intermetallic distances in a discrete metallacyclic entity is demonstrated by this type of self-assembled, triple stranded di-nuclear mesocate.

Trinuclear M$_3$L$_2$/M$_3$L$_3$ helicates: As discussed before, the ether-linked *tris*-bipyridine derivative **2** forms a trinuclear double-stranded helicates $[Cu_3 2_2]^{3+}$ in metal-directed self-assembly processes (Fig. 3) [17]. 1,10-Phenanthroline is a chelating ligand that possesses coordination features that are very similar to those of 2,2′-bipyridine. Cohen *et al.* [47-50] have introduced a series of ligand strands **13**-**16** (Fig. 7), which are analogous to the *tris*(bipyridine) derivative **2** with at least one bipyridine unit substituted by phenanthroline (or bithiophenein **16**). Ligands **13**-**16** form trinuclear double-stranded helicates $[M_3 L_2]^{3+}$ with Cu$^+$/Ag$^+$ ions. Complex $[Cu_3 13_2]^{3+}$ was characterized by X-ray structural analysis [48]. The compound with the *bis*(bipyridine)-dithiophene ligand $[Cu_3 16_2]^{3+}$ is very labile which is studied by NMR spectroscopy and electrochemistry [47]. With ligand **13**, the Ag$^+$ complex $[Ag_3 13_2]^{3+}$ and the Zn^{2+} complex $[Zn_3 13_2]^{6+}$ are also obtained [48]. The *bis*(phenanthroline)/bipyridine derivative **14** forms the corresponding Ag$^+$ helicate $[Ag_3 14_2]^{3+}$, while the analogous Ag$^+$ *tris*-(phenanthroline) helicate $[Ag_3 14_2]^{3+}$ is only stable in solution in the presence of an excess of Ag$^+$ ions. This is attributed to the increased steric hindrance of the phenanthroline compared to the bipyridine units [47,49].
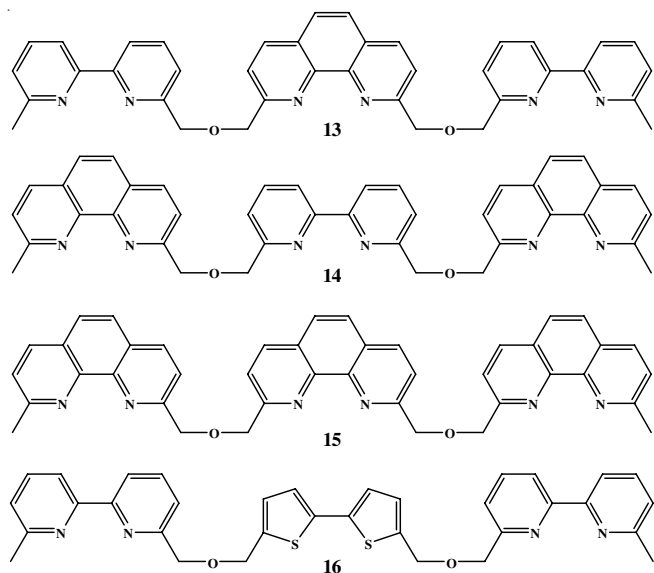

Fig. 7. Pictorial representations of ligands **13**-**16**

Besides trinuclear double stranded helicates, researchers have included a number of trinuclear triple stranded helicates in the literature. In this context, one of the early example is the *tris*(bypridine) ligand **17**, introduced by Lehn *et al*. (Fig. 8) [18,51,52]. This ligand forms trinuclear triple stranded helicates with Ni^{2+} and Fe^{2+}. The corresponding helical Ni^{2+} complex $[Ni_3 17_3]^{6+}$ crystallizes with separation of the enantiomeric helices and was structurally characterized.

Trinuclear M$_3$L$_3$ side-by-side helicates: Though a plenty of helicates with tri-nuclearity are reported in the literature, the side-by-side binding of the ligand strand around the metal centres *i.e.* alternative Λ and Δ chirality at the metal centres in
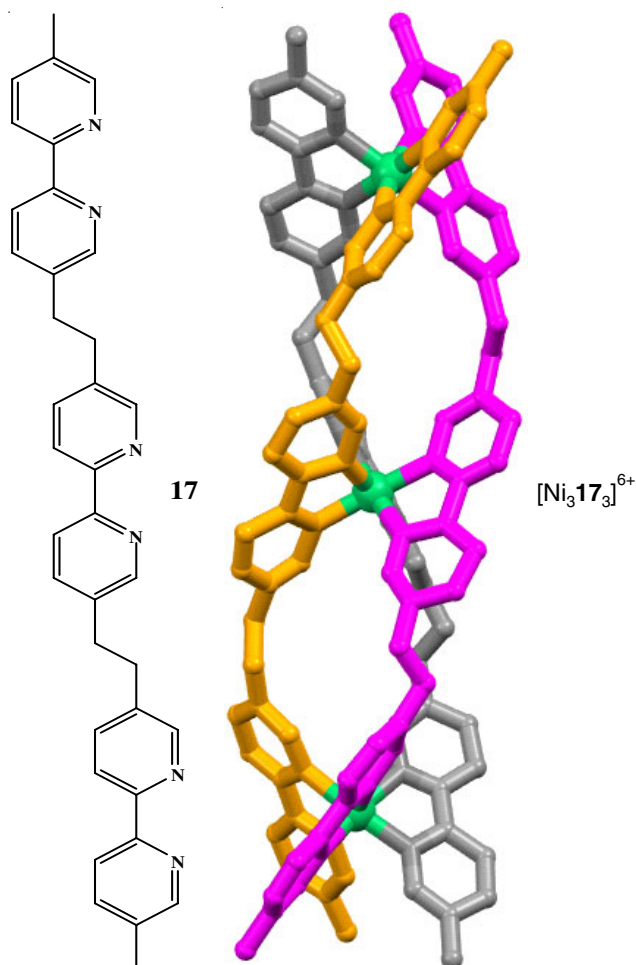
Fig. 8. Representation of ligand **17** and single crystal X-ray structure of tri-nuclear triple stranded helicate [Ni₃**17**₃]⁶⁺ with ligand **17**

cases of tri-nuclear helicates are very rare in the literature. Until now, only few examples of tri-nuclear triple-stranded helicates with alternating Δ and Λ chirality have been reported.

Reedijk *et al.* [29] reported the first case of tri-nuclear triple-stranded side-by-side helicate in 2001 with an oxo-donor pentadentate ligand **18** up on reaction with Mn^{2+} ions (Fig. 9). The three Mn^{2+} ions in the helical axis posses alternating Δ and Λ chirality and came up with an recimic mixture of two enantiomers *i.e.* 1:1 mixture ΔΔΔ and ΛΔΔ isomers in the same crystal space group. Later on, in 2009, Pardo *et al.* [30] have shown the side-by-side binding of the three nonplanar C₂-symmetric *tris*(bidentate) ligands (**19**) around the three octa-hedral Co^{2+} ions that also affords a racemic mixture of hetero-chiral tri-nuclear triple-stranded side-by-side helicate with alternating ΛΔΔ and ΔΔΔ chiralities (Fig. 9).

In 2017, Ghosh *et al.* [53] reported a linear hybrid *tris*-bidentate neutral ligand having 2,2′-bipyridine and two terminal triazolyl pyridine chelating units separated by methy-lene spacer (**20**). This ligand was used to develop a series of trinuclear triple-stranded homometallic side-by-side helicates with Fe^{2+}, Zn^{2+}, Cu^{2+} and Ni^{2+} metal ions (Fig. 9). The same group has also reported the first example of hetero-metallic trinuclear triple-stranded side-by-side helicates. The self-sorting behaviour of the hybrid ligand toward the two different metal ions selects the specific formation of [Fe₂Zn(**20**)₃](OTf)₆ and [Cu₂Zn(**20**)₃](OTf)₆, respectively (Fig. 9) [31,53]. All the heli-cates appears as 1:1 enantiomeric pairs invariably for homo and hetero metallic side-by-side helicates, resulting to an aciral helicate overall.

Conclusion

This mini-article discusses the structural aspects of a range of helicates with both homo-chiral and hetero-chiral metal
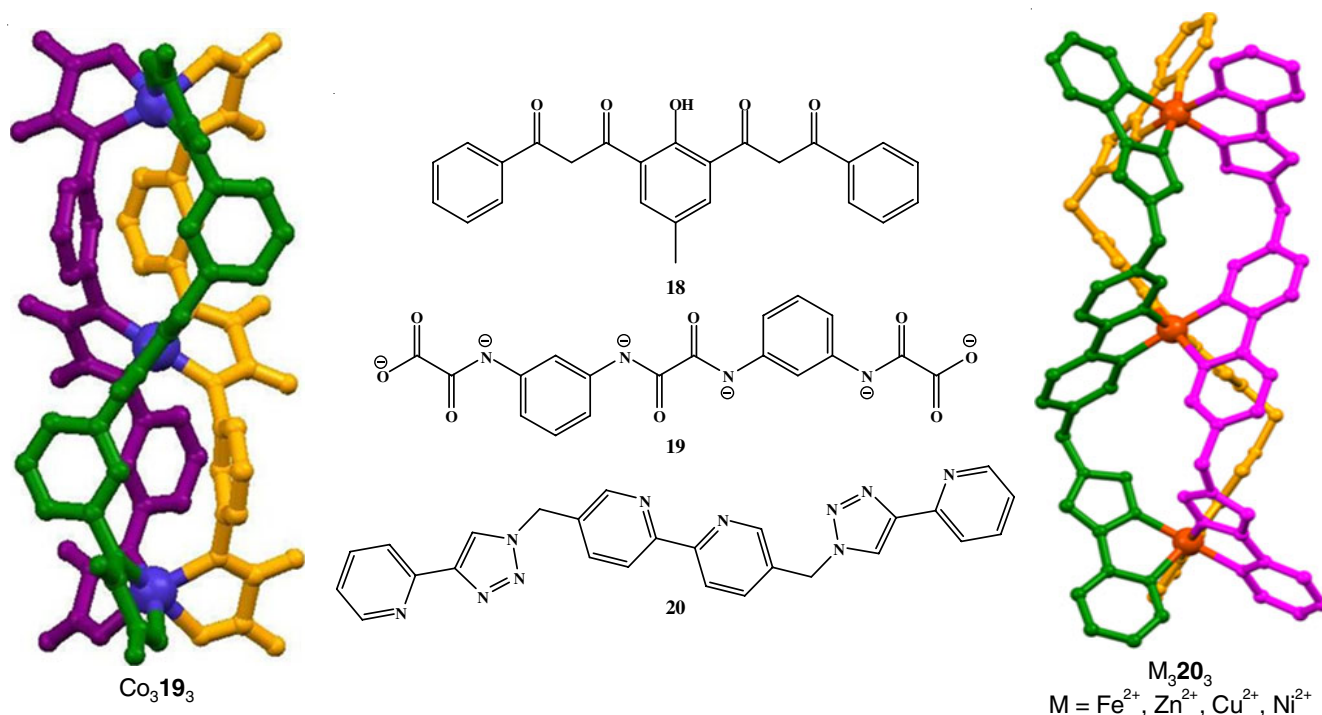

Fig. 9. Representation of ligand **18-20** and single crystal X-ray structure of tri-nuclear triple stranded side-by-side helicate [Co₃**19**₃] with ligand **19** and [Fe₃**20**₃]⁶⁺ with ligand **20**

centers. Helicates are classified based on the number of ligands wrapping around the metal centers and the number of metals for a given number of strands. In comparison to ordinary helicates, it was found that meso helicates are less common. Most of the helicates were observed as enantiomeric pairs. Nevertheless, chiral ligands were used in a few instances to synthesize stereospecific helicates. The steric interactions between ligand strands, special geometric features of the ligands and/or metals, presence of non-covalent interactions like hydrogen bonding, π–π interaction between the ligand moieties and guest templation are the controlling factors behind the formation of a specific helicate. Therefore, one should take care of these fetors during the design and synthesis of new helicates. By varying these parameters, helical architectures with fresh and innovative designs including chirality modulation are expected.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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