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 Fe2+/Co2+/Ni2+, 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
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 C₃ 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 helicate 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 (ΔΔΔ or ΔΔΔ) [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 homochiral 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 [Cu212]+ 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 [Cu33]+ and [Ag33]+ [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-cyclohexanediamine and 8-naphthylmethoxyquinoline-2-carbaldehyde (Fig. 4). The bis-bidentate ligand 4 reacts with Cu+ to form a stable helicate complex, [Cu44]+, 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](image1.png)  
**Fig. 3.** Pictorial representations of dinuclear double stranded helicate [Cu212]+ (left) with ligand 1 and trinuclear double stranded helicate [Cu33]+ (right) with ligand 2

![Fig. 4](image2.png)  
**Fig. 4.** Representation of ligands 3-4 and single crystal X-ray structure of dinuclear double stranded helicate [Cu44]+ 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 rhodotorurilic acid (5-H2) was isolated from low iron cultures of rhodorulapilimanae 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 Fe3+, Cr3+ and Al3+ ions, as reported by Raymond & Carrano [40]. Circular dichroism (CD) experiments demonstrated that both complex units of di-nuclear triple-stranded helicates [M253] (M = Fe, Cr and Al) have the same configuration. The compounds are hence triplestranded (P)-helicates. The only helicate discovered in nature prior to 1985 was the di-iron complex of rhodoturulic acid [Fe253] [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. Fe3+ and 6-H2 combine to produce a triple-stranded di-nuclear complex [Fe63], 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 [M283] helicates over mesocates with different trivalent metal ions such as Fe3+, Co3+, Mn3+, Ga3+ and In3+. 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-H2), which is separated by three methylene spacers (Fig. 6). It reacts with Ti4+ to form di-nuclear triple stranded mesocate [Ti2103]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 = Ni2+ and Co2+ in aqueous solution.

![Fig. 5. Representation of ligands 5-9 and single crystal X-ray structure of dinuclear triple stranded helicate [Ga83] with ligand 8](image-url)
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 M₃L₂/M₃L₃ helicates: As discussed before, the ether-linked tris-bipyridine derivative 2 forms a trinuclear double-stranded helicates [Cu₂2₃]⁺ 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 bithiophene 16). Ligands 13-16 form trinuclear double-stranded helicates [M₃L₂]³⁺ with Cu⁺/Ag⁺ ions. Complex [Cu₃13]³⁺ was characterized by X-ray structural analysis [48]. The compound with the bis(bipyridine)-dithiophene ligand [Cu₁6]³⁺ is very labile which is studied by NMR spectroscopy and electrochemistry [47]. With ligand 13, the Ag⁺ complex [Ag₁3]³⁺ and the Zn²⁺ complex [Zn₁3]²⁺ are also obtained [48]. The bis(phenanthroline)bipyridine derivative 14 forms the corresponding Ag⁺ helicate [Ag₁4]³⁺, while the analogous Ag⁺ tris(phenanthroline) helicate [Ag₁4]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].

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(bipyridine) ligand 17, introduced by Lehn et al. (Fig. 8) [18,51,52]. This ligand forms trinuclear triple stranded helicates with Ni²⁺ and Fe³⁺. The corresponding helical Ni²⁺ complex [Ni₁7]³⁺ crystallizes with separation of the enantiomeric helices and was structurally characterized.

Trinuclear M₃L₃ 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
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 Mn2+ ions (Fig. 9). The three Mn2+ 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 ΛΛΛ 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 octahedral Co2+ ions that also affords a racemic mixture of heterochiral tri-nuclear triple-stranded side-by-side helicate with alternating ΔΛΔ and ΛΔΛ 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 methylene spacer (20). This ligand was used to develop a series of trinuclear triple-stranded homometallic side-by-side helicates with Fe2+, Zn2+, Cu2+ and Ni2+ 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 helicates 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...
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.

**ACKNOWLEDGEMENTS**

The author thanks Chunaram Gobinda Memorial Government College and Higher Education Department of West Bengal for technical assistance.

**CONFLICT OF INTEREST**

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

**REFERENCES**
