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CHIRALITY AND STRUCTURAL MOTIF OF TRI-NUCLEAR TRIPLE-STRANDED METAL-LIGAND COORDINATION DRIVEN HELICATES

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ABSTRACT

Geometric helicity, observed in diverse architectures, can be engineered into supramolecular structures using metal coordination, hydrogen bonding, or macromolecular constraints. The chirality arising from preferential ligand orientation around metal centers distinguishes between homochiral helicates (all metal centers with the same chirality, Δ or Λ) and heterochiral helicates (alternating Δ and Λ chirality). This short review article will concentrate on coordination-driven, tri-nuclear triple-stranded helicates, exploring both homo-chiral and hetero-chiral versions.

KEYWORDS: Self-assembly, Helicate, Mesocate, Homo-chiral, Hetero-chiral

INTRODUCTION

For the past three decades, metal ion-mediated self-assembled helical compounds have remained a significant area of research [1-4]. This enduring interest stems from their potential applications in diverse fields, including anion sensing, luminescence, magnetism, chirality, molecular machines, guest recognition, and DNA binding [5-8]. Additionally, achiral meso-helical structures have shown considerable promise in information storage and processing nanotechnology, as well as in the development of molecular wires and switches [9]. The term "helicates" was first defined by J.-M. Lehn in 1987, referring to a specific type of metal complex composed of one or more ligand strands and two or more metal centers [4]. A decade later, in 1997, Piguet et al. published a prominent review that categorized helicates based on the number of metal ions and ligand strands within their structures [1]. Since then, numerous studies have explored helicate compounds featuring various metal ions and ligand strands, highlighting their intriguing applications [10-17]. This article focuses specifically on tri-nuclear triple-stranded helicates including both homo-chiral and hetero-chiral examples to illustrate the diversity of these helical architectures [18-23].

Basics of Helicate Construction

The major challenge in helicate chemistry lies in understanding the fundamental principles governing self-assembly processes. Figure 1 illustrates the key principles of helicate construction. In metal-ligand coordination helical complexes, the helical axis is defined by the line connecting two or more metal ions. Ligands form the strands of the helix by complexing with these metal ions and twisting around the axis.

The three fundamental structural elements are: the metal ion, the chelating binding site on the ligand, and the bridging unit that connects these binding sites, coordinating different metal ions. Metal ions typically exhibit preferred coordination geometries, defined by their coordination number and spatial arrangement, such as tetrahedral for Cu^{+}/Ag^{+}, octahedral for $Fe^{2+}/Co^{2+}/Ni^{2+}$, or coordination numbers of 8 or 9 for larger lanthanides. The coordination preference of the metal ion is the first element of structural control.

The second element is the ligand's binding site, defined by its denticity—the number of atoms that bind to the metal: 2 (bidentate) for bipyridines or catechols, 3 (tridentate) for terpyridines, and so on. To satisfy the metal ion's coordination preference, the total number of atoms bound to the metal is a crucial factor in helicate formation. For example, a tetrahedral ion like Cu^{+} requires two bidentate sites to form a double-stranded helical structure [4]. Conversely, an octahedral metal center necessitates three bidentate or two tridentate sites for the formation of a triple or double helix, respectively [18]. Similarly, lanthanide complexes, with their higher coordination numbers, may require three tridentate sites to achieve a triple helix via nine-coordinate metal centers [24].

Furthermore, the bridging unit connecting the chelating groups of the ligand strands plays a vital role in helical structure formation. Ideally, the bridging unit should be flexible enough to allow the ligand to wrap around the helical axis, yet sufficiently rigid to prevent the second binding site from coordinating the first metal and to ensure the transfer of helical chirality between adjacent metal centers. These three structural elements can be systematically varied through synthetic design to control the formation of desired helical structures.

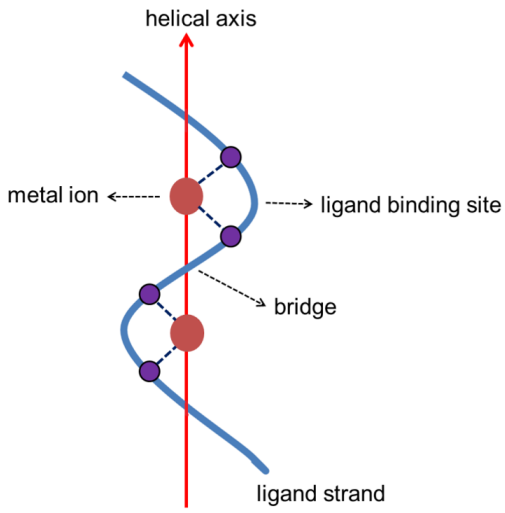

Figure 1: Structural components of helical complexes, highlighting one ligand strand.

UNDERSTANDING HELICATE CHIRALITY

In coordination chemistry, the concept of helicity has roots tracing back to the early development of Alfred Werner's coordination theory. For example, the 1,2-diaminoethane (en) ligands in $[Co(en)_3]^{3+}$ can twist either clockwise (Δ) or anticlockwise (Λ) around the complex's C3 symmetry axis [25]. Consequently, the chirality of helicates arises from the helical wrapping of ligands around metal centers.

Dinuclear helicates are classified into two types based on the chirality at the metal centers. Firstly, homochiral helicates exhibit the same configuration (either Δ or Λ) at both metal centers [26-28]. Secondly, heterochiral helicates, where the metal centers alternate between Δ and Λ configurations are also possible [29-31]. These heterochiral arrangements, possessing a mirror plane at the helicate's center, result in achiral meso-forms, known as meso-helicates or mesocates. Therefore, the deliberate formation of helicate structures with ligands helically wrapped around homochiral (Δ or Λ) metal ions requires careful selection of bridging ligands and metal ions. Conversely, side-by-side binding of ligands around metal centers with opposite chirality (Δ and Λ) yields achiral mesocate structures.

Extending dinuclear helicates to trinuclear forms yields two distinct types. Firstly, homochiral helicates (ΔΔΔ or ΛΛΛ) result from a continued helical wrapping of the ligand strand along the helical axis as shown in figure 2(a) [18-19]. Secondly, adding a metal center to a dinuclear mesocate can produce a trinuclear helicate with alternating Δ and Λ chirality (ΔΛΔ or ΛΔΛ) figure 2(b) [20-23]. This odd number of metal centers renders the overall complex chiral. However, in these cases, the ligands adopt a parallel, zigzag binding mode rather than a helical wrap, leading to their classification as side-by-side helicates.

It's important to note that when the ligand strand lacks chiral centers, homochiral helicates typically form as a racemic mixture of enantiomers (e.g., a 1:1 mixture of ΔΔΔ and ΛΛΛ helicates). Nevertheless, spontaneous resolution during crystallization can sometimes yield a single helical isomer. Alternatively, introducing chiral substituents onto the ligand provides a reliable method for synthesizing specific chiral helicates (ΔΔΔ or ΛΛΛ).

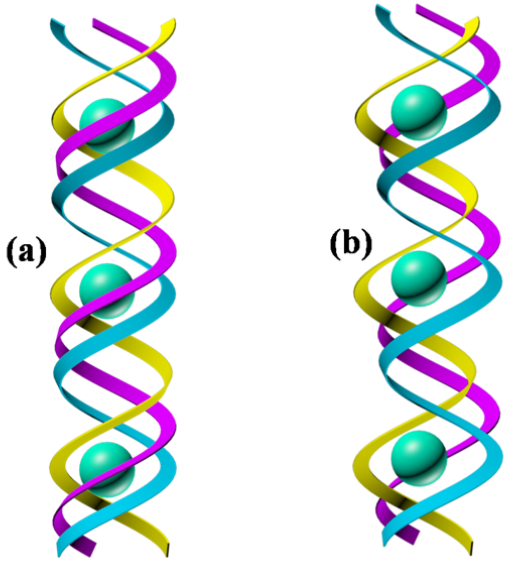

Figure 2: Pictorial representation of Homo-chiral (a) and Hetero-chiral (b) helicates.

Homo-chiral Tri-nuclear Triple-stranded (M_3L_3) Helicate: Researchers have included a number of trinuclear triple stranded helicates in the literature [1, 18-23]. In this context, one of the early example is the tris(bypridine) ligand L1, introduced by Lehn in 1998 (Figure 3) [18]. This ligand forms trinuclear triple stranded helicates with Ni^{2+} and Fe^{2+}. The corresponding helical Ni^{2+} complex $[Ni3L13]^{6+}$ crystallizes with separation of the enantiomeric helices and was structurally characterized. The complex $[Ni3L13]^{6+}$ consists of three ligand strands wrapped around three Ni(II) ions, forming a trinuclear triple-helical structure, as depicted in Figure 3.

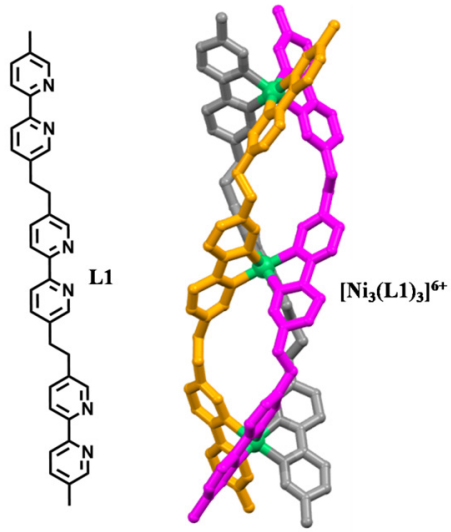

Figure 3: Representation of ligand **L1** and single crystal X-ray structure of tri-nuclear triple stranded helicate $[Ni_3\mathbf{L1}_3]^{6+}$ with ligand **L1**.

In recent times, Gütz et al. prepared a tris(bipyridine) ligand, **L2**, featuring two BINOL (2,2'-dihydroxy-1,1'-binaphthyl) units, which act as stereogenic centers [19]. This ligand was synthesized in two enantiomerically pure forms. When coordinated with iron(II) ions, the (P,P)-**L2** enantiomer undergoes a completely diastereoselective self-assembly process, yielding a D3-symmetric (Δ,Δ,Δ)-triple-stranded trinuclear helicate (Figure 4). Similarly, the (M,M)-**L2** enantiomer forms the corresponding (Λ,Λ,Λ) helicate.

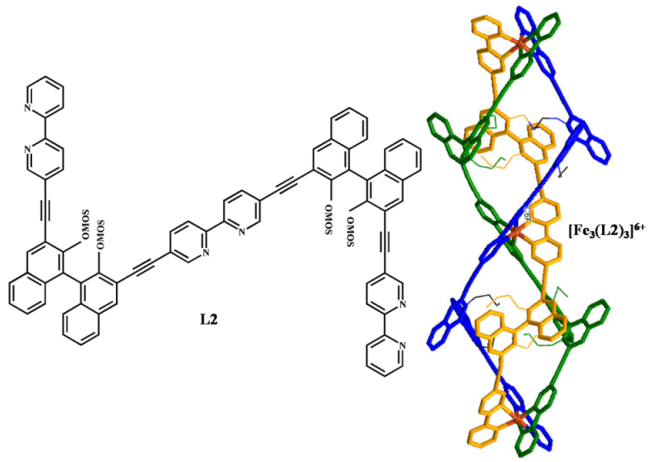

Figure 4: Representation of ligand **L2** and single crystal X-ray structure of tri-nuclear triple stranded helicate $[Ni3L23]^{6+}$ with ligand **L2**.

Hetero-chiral Tri-nuclear Triple-stranded (M_3L_3) Helicate: Although trinuclear helicates are well-represented in the literature, the occurrence of side-by-side ligand binding, characterized by alternating Λ and Δ chirality at the metal centers, is rare. Consequently, only a small number of trinuclear triple-stranded helicates displaying this specific structural motif have been reported.

In 2001, Reedijk and co-workers reported the first example of a trinuclear triple-stranded side-by-side helicate [20]. This was achieved using an oxo-donor pentadentate ligand L3 reacting with Mn^{2+} ions (Figure 5). The three Mn^{2+} ions along the helical axis exhibited alternating Δ and Λ chirality, resulting in a racemic mixture of ΔΛΔ and ΛΔΛ isomers within the same crystal space group. Subsequently, in 2009, Pardo et al. demonstrated side-by-side binding of three nonplanar C_2-symmetric tris(bidentate) ligands **L4** around three octahedral Co^{2+} ions [21]. This also yielded a racemic mixture of heterochiral trinuclear triple-stranded side-by-side helicates with alternating ΛΔΛ and ΔΛΔ chiralities (Figure 5).

Ghosh and co-workers recently synthesized a linear hybrid tris-bidentate neutral ligand (20) featuring 2,2'-bipyridine and two terminal triazolyl pyridine chelating units, linked by a methylene spacer. This ligand facilitated the formation of a series of trinuclear triple-stranded homometallic side-by-side helicates with Fe^{2+}, Zn^{2+}, Cu^{2+}, and Ni^{2+} ions (Figure 5) [22-23]. Notably, they also reported the first examples of heterometallic trinuclear triple-stranded side-by-side helicates. The ligand exhibited self-sorting behavior, selectively forming $[Fe_2Zn(\mathbf{L5})_3](OTf)_6$ and $[Cu_2Zn(\mathbf{L5})_3](OTf)_6$ when exposed to the respective metal ion combinations. In both homometallic and heterometallic cases, the helicates formed as 1:1 enantiomeric pairs, resulting in overall achiral structures.

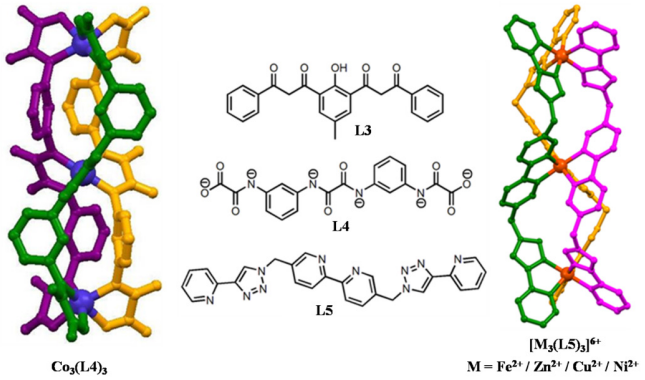

Figure 5: Representation of ligand **L3**, **L4** and **L5** and single crystal X-ray structure of tri-nuclear triple stranded side-by-side helicate [Co3L43] with ligand **L4** and $[Fe_3\mathbf{L5}_3]^{6+}$ with ligand **L5**.

CONCLUSIONS

This article reviews the structural features of trinuclear triple-stranded helicates, encompassing both homochiral and heterochiral examples. Notably, heterochiral helicates of this type are significantly less prevalent than their homochiral counterparts, with only four reported instances. The formation of these helicates is dictated by steric interactions between ligand strands, the geometric properties of the ligands and metal ions, and non-covalent interactions like hydrogen bonding and π-π stacking. These factors are crucial considerations in the design and synthesis of novel helicates. Manipulating these parameters offers a pathway to innovative helical architectures and the modulation of helicity.

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REFERENCES

1. Piguet, C., Bernardinelli, G. and Hopfgartner, G. (1997). Helicates as Versatile Supramolecular Complexes, Chemical Reviews, 97(6), p. 2005-2062.
2. Sun, W.-Y., Yoshizawa, M., Kusukawa, T. and Fujita, M. (2002). Multicomponent metal–ligand self-assembly, Current Opinion in Chemical Biology, 6(6), p. 757-764.
3. Yashima, E., Ousaka, N., Taura, D., Shimomura, K., Ikai, T. and Maeda, K. (2016). Supramolecular Helical Systems: Helical Assemblies of Small Molecules, Foldamers, and Polymers with Chiral Amplification and Their Functions, Chemical Reviews, 116(22), p. 13752-13990.
4. Lehn, J. M., Rigault, A., Siegel, J., Harrowfield, J., Chevrier, B. and Moras, D. (1987). Spontaneous assembly of double-stranded helicates from oligobipyridine ligands and copper(I) cations: structure of an inorganic double helix, Proceedings of the National Academy of Sciences, 84(9), p. 2565-2569.
5. Oleksi, A., Blanco, A. G., Boer, R., Usón, I., Aymamí, J., Rodger, A., Hannon, M. J. and Coll, M. (2006). Molecular Recognition of a Three-Way DNA Junction by a Metallosupramolecular Helicate, Angewandte Chemie International Edition, 45(8), p. 1227-1231.

6. Lavalette, A., Tuna, F., Clarkson, G., Alcock, N. W. and Hannon, M. J. (2003). Aggregation of metallo-supramolecular architectures by metallo-assembled hydrogen bonding sites, Chemical Communications21), p. 2666-2667.
7. Harding, L. P., Jeffery, J. C., Riis-Johannessen, T., Rice, C. R. and Zeng, Z. (2004). Anion control of ligand self-recognition in a triple helical array, Chemical Communications6), p. 654-655.
8. Amendola, V., Fabbrizzi, L., Pallavicini, P., Sartirana, E. and Taglietti, A. (2003). Monitoring the Redox-Driven Assembly/ Disassembly of a Dicopper(I) Helicate with an Auxiliary Fluorescent Probe, Inorganic Chemistry, 42(5), p. 1632-1636.
9. Mochizuki, T., Nogami, T. and Ishida, T. (2009). Ferromagnetic Superexchange Coupling through a Diamagnetic Iron(II) Ion in a Mixed-Valent Iron(III, II, III) meso-Helicate, Inorganic Chemistry, 48(5), p. 2254-2259.
10. Swiegers, G. F. and Malefetse, T. J. (2002). Classification of coordination polygons and polyhedra according to their mode of self-assembly. 2. Review of the literature, Coordination Chemistry Reviews, 225(1), p. 91-121.
11. Miyake, H. and Tsukube, H. (2012). Coordination chemistry strategies for dynamic helicates: time-programmable chirality switching with labile and inert metal helicates, Chemical Society Reviews, 41(21, p. 6977-6991.
12. Boiocchi, M. and Fabbrizzi, L. (2014). Double-stranded dimetallic helicates: assembling–disassembling driven by the CuI/ CuII redox change and the principle of homochiral recognition, Chemical Society Reviews, 43(6), p. 1835-1847.
13. Saalfrank, R. W., Maid, H. and Scheurer, A. (2008). Supramolecular Coordination Chemistry: The Synergistic Effect of Serendipity and Rational Design, Angewandte Chemie International Edition, 47(46), p. 8794-8824.
14. Williams, A. (1997). Helical Complexes and Beyond, Chemistry – A European Journal, 3(1), p. 15-19.
15. Hannon, M. J. and Childs, L. J. (2004). Helices and Helicates: Beautiful Supramolecular Motifs with Emerging Applications, Supramolecular Chemistry, 16(1), p. 7-22.
16. Constable, E. C. (2013). Stereogenic metal centres – from Werner to supramolecular chemistry, Chemical Society Reviews, 42(4), p. 1637-1651.
17. Akhuli, B. (2024). Metal-Ligand Coordination Driven Di/Tri-nuclear Helicate and Mesocate: A Brief Review, Asian Journal of Chemistry, 36(5), p. 1009-1016.
18. Hasenknopf, B., Lehn, J.-M., Boumediene, N., Leize, E. and Van Dorsselaer, A. (1998). Kinetic and Thermodynamic Control in Self-Assembly: Sequential Formation of Linear and Circular Helicates, Angewandte Chemie International Edition, 37(23), p. 3265-3268.
19. Gütz, C., Hovorka, R., Struch, N., Bunzen, J., Meyer-Eppler, G., Qu, Z.-W., Grimme, S., Topić, F., Rissanen, K., Cetina, M., Engeser, M. and Lützen, A. (2014). Enantiomerically Pure Trinuclear Helicates via Diastereoselective Self-Assembly and Characterization of Their Redox Chemistry, Journal of the American Chemical Society, 136(33), p. 11830-11838.
20. Aromí, G., Carrero Berzal, P., Gamez, P., Roubeau, O., Kooijman, H., Spek, A. L., Driessen, W. L. and Reedijk, J. (2001). A Unique Asymmetric [Mn$\rm{^{II}_{3}}$] Triple-Stranded Helicate from a Symmetric Pentadentate Ligand, Angewandte Chemie International Edition, 40(18), p. 3444-3446.
21. Dul, M.-C., Pardo, E., Lescouëzec, R., Chamoreau, L.-M., Villain, F., Journaux, Y., Ruiz-García, R., Cano, J., Julve, M., Lloret, F., Pasán, J. and Ruiz-Pérez, C. (2009). Redox Switch-Off of the Ferromagnetic Coupling in a Mixed-Spin Tricobalt(II) Triple Mesocate, Journal of the American Chemical Society, 131(41), p. 14614-14615.
22. Akhuli, B., Cera, L., Jana, B., Saha, S., Schalley, C. A. and Ghosh, P. (2015). Formation and Transmetalation Mechanisms of Homo- and Heterometallic (Fe/Zn) Trinuclear Triple-Stranded Side-by-Side Helicates, Inorganic Chemistry, 54(9), p. 4231-4242.
23. Jana, B., Cera, L., Akhuli, B., Naskar, S., Schalley, C. A. and Ghosh, P. (2017). Competitive Transmetalation of First-Row Transition-Metal Ions between Trinuclear Triple-Stranded Side-by-Side Helicates, Inorganic Chemistry, 56(20), p. 12505-12513.
24. Piguet, C., Hopfgartner, G., Williams, A. F. and Bünzli, J.-C. G. (1995). Self-assembly of the first heterodinuclear d–f triple helix in solution, Journal of the Chemical Society, Chemical Communications, (4), p. 491-493.
25. von Zelewsky, A. (2014). Stereochemistry of coordination compounds. From alfred werner to the 21st century, Chimia (Aarau), 68(5), p. 297-298.
26. Boiocchi, M., Brega, V., Ciarrocchi, C., Fabbrizzi, L. and Pallavicini, P. (2013). Dicopper Double-Strand Helicates Held Together by Additional π-π Interactions, Inorg. Chem., (52), p.10643.
27. Albrecht, M., Isaak, E., Baumert, M., Gossen, V., Raabe, G. and Frohlich, R. (2011). "Induced fit" in chiral recognition: epimerization upon dimerization in the hierarchical self-assembly of helicate-type titanium(IV) complexes, Angew Chem Int Ed Engl, 50(12), p. 2850-2853.
28. Howson, S. E., Bolhuis, A., Brabec, V., Clarkson, G. J., Malina, J., Rodger, A. and Scott, P. (2012). Optically pure, water-stable metallo-helical 'flexicate' assemblies with antibiotic activity, Nat. Chem., (4), p. 31.
29. Raja, M., Iyer, R. G., Gwengo, C., Reger, D. L., Pellechia, P. J., Smith, M. D. and Pascui, A. E. (2013). Design, Synthesis, and Structural Characterization of a New Class of Ferrocene-Containing Heterometallic Triple-Stranded Helicates, Organometallics, (32), p. 95.
30. Djeda, R., Desmarets, C., Chamoreau, L. M., Li, Y., Journaux, Y., Gontard, G. and Amouri, H. (2013). Meso-Helicates with Rigid Angular Tetradentate Ligand: Design, Molecular Structures, and Progress Towards Self-Assembly of Metal-Organic Nanotubes, Inorg. Chem., (52), p. 13042.
31. Dul, M.-C., Pardo, E., Lescouëzec, R., Chamoreau, L.-M., Villain, F., Journaux, Y., Ruiz-García, R., Cano, J., Julve, M., Lloret, F., Pasán, J. and Ruiz-Pérez, C. (2009). Redox Switch-Off of the Ferromagnetic Coupling in a Mixed-Spin Tricobalt(II) Triple Mesocate, Journal of the American Chemical Society, 131(41), p. 14614-14615.