

Helicates: Supramolecular Architectures via Metal Ion-Directed Assembly

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Helical structures are often found in nature, examples of which include deoxyribonucleic acid (DNA), protein α -helices, and collagen. Helices may hold their particular shape through conformational restrictions, hydrogen bonding, or metal ion coordination. The term “helicates,” coined by Lehn, J.-M. *et al.* in 1987, refers specifically to those formed by metal ion coordination.¹ Helicates are typically composed of one to four intertwining strands, with some highly twisted structures extending into the realm of molecular knots. The focus here will be on double and triple stranded helicates, with an overview of classic bipyridine (bipy) and terpyridine (terpy) structures and representative examples of recent work, including sensor applications.

Work on helicates was occurring before the term was coined, although expansion in the field did not occur until the late 1980’s followed by rapid growth in the late 1990’s.² Much of the early work, and some later work, involved the use of bipyridine and terpyridine moieties in the assembled ligands. These structures readily interact with a variety of metal ions allowing multiple topologies to be generated. Building on these basic structures, four recent articles from the field will be discussed. These include works by Constable, E. C. *et al.* and Quinodoz, B. *et al.* (continuations of classical topological studies), as well as those of Bokolinis, G. *et al.* and Oleksi, A. *et al.*, (showing applications of helicates in sensing).³⁻⁶

Constable, E. C. *et al.* created a hairpin helicate that lies halfway between double stranded helicates and trefoil knots in structure. This helicate is based loosely on a terpy structure with a spacer linking the two chelating halves. A spacefilling version of the crystal structure is seen below in Figure 1. Quinodoz, B. *et al.* created CHIRAGEN type ligands with ferrocene linkers that formed complexes with Cu^{1+} , Ag^{1+} and Zn^{2+} . The X-ray structure of one Cu^{1+} complex is shown in Figure 2.

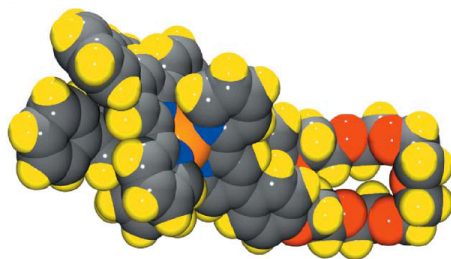


Figure 1: Spacefilling model of the cation in $[\text{Cu}_2(\text{IX})][\text{PF}_6]_3 \cdot 2.5\text{Me}_2\text{CO}$.³

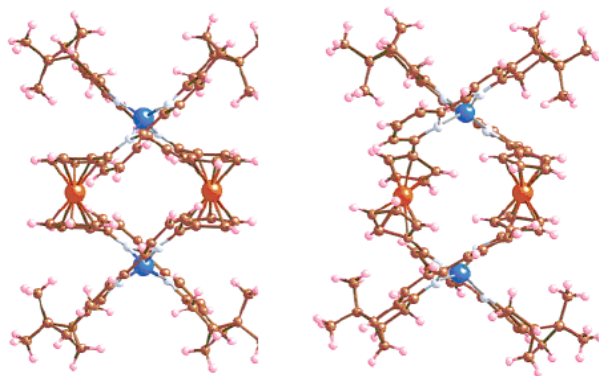


Figure 2: Two X-ray structures derived from the same compound, $[\text{Cu}_2(\text{L})_2](\text{PF}_6)_2$.⁴ Picture a less-than sign overlapping with a greater than sign, with Cu^{1+} ions at the intersection points.

Since many topologies have now been explored, it has become possible to create several sensors, knowing the shapes and behaviors of many compounds as well as having the ability to tailor their size and shape for specific applications. Bokolinis, G. *et al.* created a helicate with potential use as a colorimetric Ba^{2+} sensor, albeit with limited selectivity and sensitivity.⁵ The Ba^{2+} complexed form is shown in Figure 3. Oleksi, A. *et al.* discovered that a helicate could specifically recognize a three-way DNA junction.⁶ Several diseases have been associated with three-way junctions, so the authors propose using the specificity of the helix to direct drugs towards these junctions. The $[\text{Fe}_2\text{L}_3]^{4+}$ -DNA complex is shown below in Figure 4.

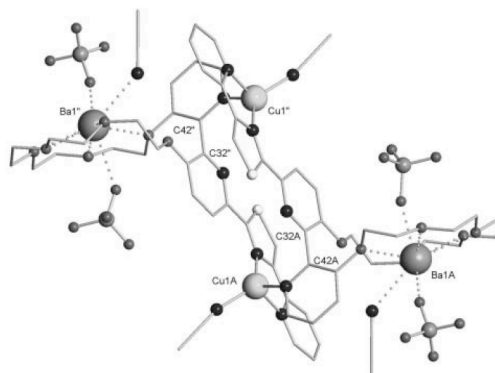


Figure 3: $[\text{Cu}_2(\text{L})_2\text{Ba}](\text{ClO}_4)_4(\text{MeCN})_4^{2+}$ complex shown in the side-by-side form (binding of Ba^{2+} by the 18-crown-6 moiety results in loss of helical character and subsequent color change).⁵

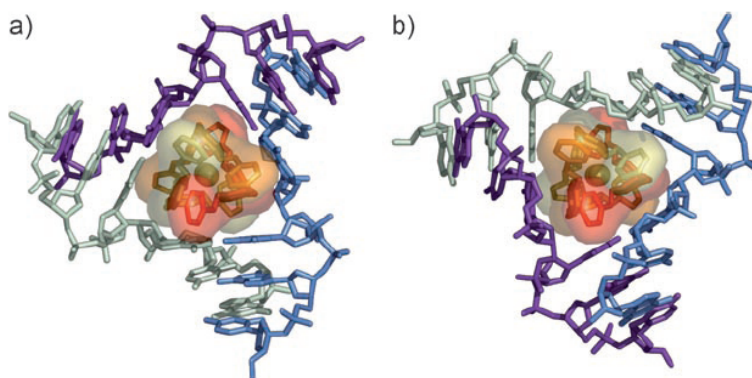


Figure 4: $[\text{Fe}_2\text{L}_3]^{4+}$ -DNA complex. a. Major groove side. b. Minor groove side.⁶

A substantial amount of progress has been made in the field of helicates since they were first named by Lehn, J.-M. *et al.* These advances came not only in the range of available structures, but also in the development of sensors. The study of different structures will be ongoing with new applications being developed congruently, as a greater understanding of the available topologies leads to new ideas in sensing and other potential applications. The four examples chosen, although not directly linked, all rely on the same basic principles and provide an overview of current work in this field.

References

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