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Triple-Stranded Cluster Helicates for the Selective Catalytic Oxidation of C−H Bonds

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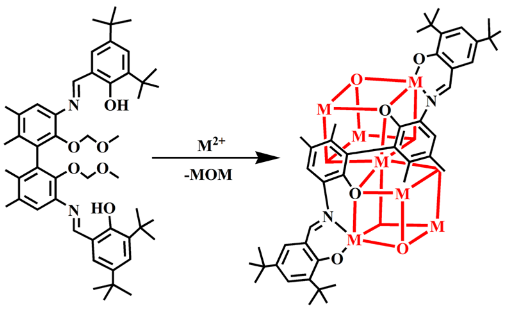
Ⓢ *Supporting Information*

ABSTRACT: Triple-stranded cluster helicates with heptametallic dicubane cores are synthesized by entrapping metals in the cavities of linear triple helicates based on a C_2-symmetrical hexadentate Schiff-base ligand of ortho-substitued biphenol. The helicates are stable in both the solution and solid states, and the copper species could selectively catalyze the oxidation of C−H bonds of alkanes to ketones.

Helical structures are ubiquitous in nature, particularly in biomacromolecules such as peptides and DNA, and are integral to various biological functions.[1] Their prominent functions have motivated chemists to make artificial helical architectures.[2,3] Of particular interest is the design and assembly of multistranded helicates.[3] Helicates are efficient units for constructing novel materials, devices, and machines with tunable functions and properties such as chirality, luminescence, magnetic exchange, and DNA binding.[4] Because the intrinsically important physical, chemical, and biological properties of clusters were transferred into helicates, all of these potential applications could undergo remarkable development.[5] Helicates are generally constructed from flexible oligodentate strands and transition metals.[3] However, complications associated with the simultaneous coordination of more than three metal ions with organic strands have limited most helicates to di- or trinuclear species. There are no efficient synthetic routes to cluster helicates, and so only a very few examples of such helicates have been made.[6]

Biphenol and its derivatives exhibit intrinsic C_2-symmetric twisted conformations and are ideal platforms for the synthesis of helical species.[7] We have developed pyridyl- or carboxylic-functionalized 1,1′-biphenol-based ligands through which a variety of helical coordination polymers or chiral metal−organic frameworks constituted by helicates can be assembled,[7a,8] In this work, we report the synthesis and characterization of two triple-stranded helicates consisting of corner-sharing heptanuclear dicubane clusters and demonstrate the capability of the copper species to selectively catalyze oxidation of C−H bonds.

Scheme 1. Synthesis of Helicates 1 and 2



L-(2MOM-2H) $[M_7(OH)_2L_3]$·Guest M = Cu **1**, Zn **2**

[a]Only one ligand is shown in the product.

The ligand **L**-(2MOM-2H) (MOM = methoxymethyl) could be readily synthesized by condensation of 3,3′-diamino-5,5′,6,6′-tetramethyl-2,2′-bis(methoxymethoxy)-1,1′-biphenyl and 3,5-di-*tert*-butyl salicylaldehyde. Heating metal(II) salts and the ligand **L**-(2MOM-2H) (2:1 molar ratio) in aqueous organic solvents afforded single crystals of $[Cu_7(OH)_2L_3]·2DMF·2H_2O$ (**1**; Scheme 1) and $[Zn_7(OH)_2L_3]·6DMF·2H_2O$ (**2**) in good yield. Both of the air-stable products are soluble in common organic solvents such as CH_2Cl_2 and tetrahydrofuran. They were formulated based on elemental analysis, IR, and mass spectrometry (MS). The stability of the helicates in solution is demonstrated by electrospray ionization mass spectrometry (ESI-MS), which gave prominent peaks for $[Cu_7(OH)_2L_3 + 4H]^+$ at m/z 2579.9 and $[Zn_7(OH)_2L_3 + K - 5H]^+$ at m/z 2616.8.

The ^1H and ^{13}C NMR spectra of **2** show one clear set of proton signals as the free ligand, most of which are shifted upfield slightly. The number of signals indicated that the C_2 symmetry of the biphenyl ligand is maintained in the helicate complex. The disappearance of the signals around 2.86−4.88 ppm of MOM groups suggests that the MOM group was completely removed during the crystal growth process, whereas the disappearance of the −OH protons supported deprotonation of the phenolic hydroxyl group and complexation of the metal and ligand. The UV−vis spectrum of **L**-(2MOM-2H) in $CHCl_3$ shows three large peaks centered near 290, 341, and 361 nm due to $\pi-\pi^*$ transitions of aromatic rings and azomethine chromophore groups. Upon complexation with metal ions, the peaks assigned to the same transitions were observed at 295, 439, and 461 nm for **1** and 315, 437, and 457 nm for **2**, respectively. There is one new band around 646 nm for **1**, which was assigned to the d−d transition of Cu^{II} ions.[9] The ligand is weakly luminescent in $CHCl_3$ with a signal at 412 nm under 290 nm excitation. The

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luminescence is significantly enhanced in **2** with a signal at 511 nm but is completely quenched in **1**.

Single-crystal X-ray diffraction of **1** and **2** unambiguously revealed the formation of triple-stranded cluster helicates (Figure 1). **1** crystallizes in the triclinic space group $P\bar{1}$, with one whole formula unit in the asymmetric unit, while **2** crystallizes in the monoclinic space group $C2/c$, with half of the formula unit in the asymmetric unit and a crystallographic C_2 axis passing through the central metal. Both **1** and **2** can be viewed as a linear hexanuclear triple-stranded helicate enclosing one metal ion in the cavity. The metal ions are engaged in two M_4O_4 distorted cubanes sharing one metal ion. The six outer metal ions each adopt a distorted square-pyramidal geometry with the equatorial plane occupied by the NO_3 donors of one **L** ligand and one OH group and the apical position by one O atom of another **L** ligand, whereas the central metal ion adopts a distorted octahedral geometry by coordinating to three N and three O atoms from three **L** ligands. In the cubane unit, the adjacent M−M distances range from 3.1116(1) to 3.3036(1) Å for **1** and from 3.1089(1) to 3.2472(1) Å for **2**. All three ligands possess the same *R* conformation, and each ligand coordinates to four metal ions by using its two tridentate NO_2 donors and two biphenolate O atoms. The bulk of the biphenol moieties are pointing outward from the cluster core, and the dihedral angles between the two twisted phenyl rings of the **L** ligands are 74.1−81.5° for **1** and 76.8−79.1° for **2**.

This arrangement of the dicubane cluster and hexadentate **L** ligands thus results in a *P*-configured triple-stranded helicate with overall lengths of 24.1 and 24.5 Å and maximum widths of 16.1 and 15.9 Å for **1** and **2**, respectively. The three pairs of *tert*-butyl groups of the ligand **L** are organized such that they cover two terminal sides of the helicate, thereby generating two hydrophobic pockets, each of which is occupied by one *N*,*N*-dimethylformamide (DMF) molecule. A metal cluster with a coordinatively unsaturated metal center in a hydrophobic pocket holds potential to mimic the active site of a metalloenzyme; the metal site can bind the substrates, and the hydrophobic pocket can recognize the substrates.[10] There is, however, only a handful of such complexes that have been reported.[11]

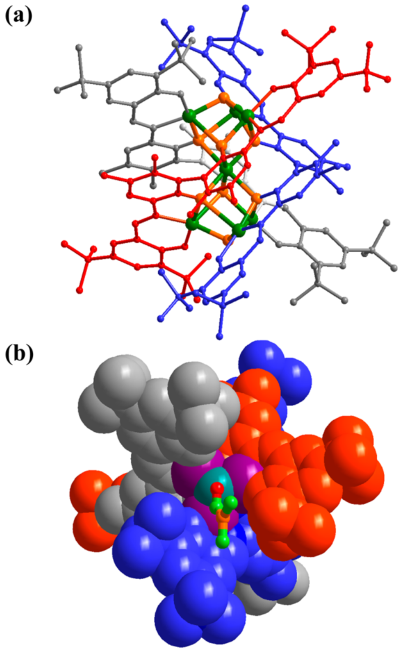


Figure 1. (a) View of the triple-stranded heptametallic helicate in **1** and **2**. (b) Space-filling mode of the helicate with an included DMF molecule.

The highly stable framework and intriguing cluster structure presented by **1** have prompted us to explore its catalytic oxidation chemistry. **1** was found to exhibit impressive catalytic activity in the peroxidative oxidation of alkanes to the corresponding alcohols and ketones. In our model reaction, we converted cyclopentane into cyclopentanone and cyclopentanol in acetonitrile using an excess of 3 M aqueous H_2O_2 as the oxidizing agent at 55 °C. The gas chromatography (GC) trace of the reaction mixture showed the formation of cyclopentanone in a yield of 12.15% along with a trace amount of cyclopentanol, when the molar ratio of catalyst to substrate was 1:125.

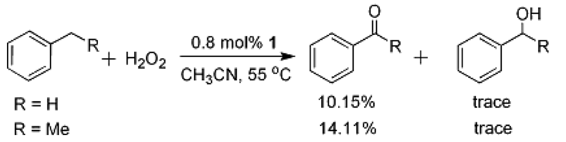
Under otherwise identical conditions, we could also convert cyclohexane, cyclooctane, toluene, and ethylbenzene to their corresponding ketones and alcohols (Table 1 and Scheme 2).

Table 1. Peroxidative Oxidation of Alkanes Catalyzed by 1

					yield (%) of product[b]		
entry	substrate	T/°C	$n(H_2O_2)/n(\text{catalyst})$	time/h	**4**	**5**	total[c]
1	**3a** (n = 1)	25	3360	72	3.55	trace	3.55
2	**3a**	55	670	4	10.43	trace	10.43
3	**3a**	55	3360	6	12.15	trace	12.15
4	**3b** (n = 2)	25	3360	72	3.12	3.04	6.16
5	**3b**	55	670	4	8.24	7.98	16.22
6	**3b**	55	3360	6	10.42	10.33	20.75
7	**3c** (n = 4)	25	3360	72	4.51	trace	4.51
8	**3c**	55	670	4	8.86	trace	8.86
9	**3c**	55	3360	6	15.23	trace	15.23
10	**3b**	55	N/A[d]	72	N.D	N.D	N.D[e]

[a]Reaction conditions: catalyst (15.3−22.1 mg), H_2O_2 (3.97−28.76 mmol), and substrate (0.1 mL). [b]Moles of product/100 mol of alkane. [c]Ketone + alcohol. [d]No catalyst but excess H_2O_2 was added. [e]Not detected by GC−MS.

Scheme 2. Peroxidative Oxidation of Toluene and Ethylbenzene Catalyzed by 1



The oxidation of cyclohexane led to a mixture product of cyclohexanol (10.33%) and cyclohexanone (10.42%) (entry 6 in Table 1), whereas cyclooctane gave its corresponding ketone as the predominant product (4.51−15.23% yield) with a trace amount of alcohol (entries 7−9 in Table 1). Besides, the oxidation of toluene and ethylbenzene gave their corresponding ketones as the main products (11−15% yield) with a trace amount of alcohol. Although yields of up to 20.75% for **1** are moderate in the oxidation of inert alkanes, the selectivities for the oxidation of cyclopentane and cyclooctane are fairly comparable with those of documented high-performing systems including polynuclear copper complexes.[12] A further study on the catalytic performance of this helicate and related analogues and understanding the origin of the catalytic selectivity is still underway.

In experiments in which the concentration of H_2O_2 was varied, comparable yields were obtained, whereas further increasing the amount of the oxidant led to a decrease in the yield. Decreasing the reaction temperature to 25 °C also led to a decrease in the yield. However, the molar ratio of products ketone to alcohol with **1** did not change when lower amounts of oxidant were applied to the substrate and/or the reaction time was decreased (entry 5, Table 1). This result suggests that the above oxidation reactions may proceed by a radical-type mechanism. This is supported by the fact that significantly decreased yields were obtained if a carbon-radical trap such as $CBrCl_3$ or 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) was subjected to the reactions. $CBrCl_3$ almost completely suppresses the formation of the oxidation products, while TEMPO results in around 90% suppression of the alkane.[13] This radical mechanism was also supported by the fact that helicate **2** could not promote C−H bond oxidation because the zinc cluster could not generate highly reactive hydroxyl radicals.

Upon completion of the oxidation of cyclohexane, the catalyst **1** could be recovered by adding ether to the reaction mixture. The recovered sample can be used repeatedly for the following three runs without loss of catalytic activity (yields: 20.75, 20.24, and 20.11%, respectively). To confirm that the helicate does not fragment during the catalytic reaction, we compared the starting catalyst to those after reaction by employing UV−vis and ESI-MS. The recovered compound shows absorption bands identical with those of the starting species. MS analysis also confirms that the clusters after reaction show a prominent peak for $[Cu_7(OH)_2\mathbf{L}_3 + 5H]^+$ at *m/z* 2581.2. Taken together, these results confirm that the cluster helicate remains intact during the reaction. The ready tunability of such a modular approach based on Schiff-base metal complexes holds promise for constructing robust helicates with unique catalytic activity and selectivity.

In conclusion, we have prepared triple-stranded cluster helicates with a heptametallic dicubane core based on a C_2-symmetrical hexadentate Schiff-base ligand of ortho-substituted biphenol. The copper species could selectively catalyze the oxidation of alkenes to ketones. The modular nature of the present synthetic approach should allow for the construction of diverse helicates with unique cluster cores and novel properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b01828.

Experimental details and spectral data (PDF)

Crystallographic file in CIF format (CIF)

Crystallographic file in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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