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Systems Chemistry

Selective Assembly and Disassembly of a Water-Soluble $Fe_{10}L_{15}$ Prism**

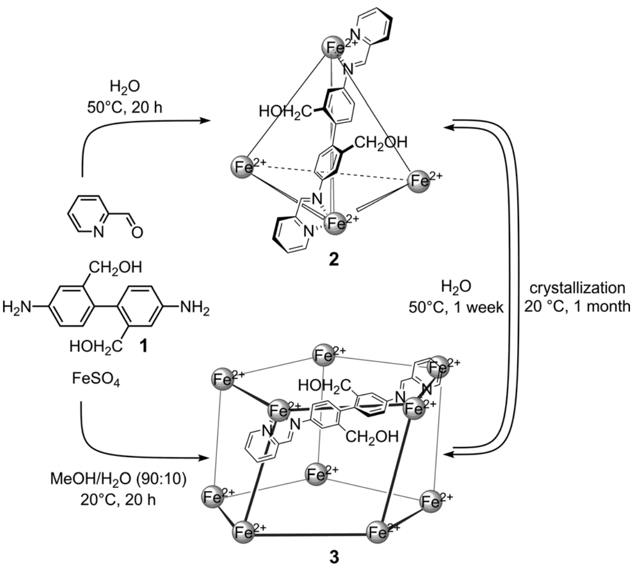
*Salvatore Zarra, Jack K. Clegg, and Jonathan R. Nitschke**

Significant attention has been recently given to the synthesis of new metal–organic architectures, which have found applications in molecular recognition, reactivity modulation, and catalysis.[1] The assembly of structures such as tetrahedra[2] and cubes[3] is increasingly practical for metal–organic chemists. However, more complex architectures remain elusive.[4] Others[5] and our group[6] have prepared a variety of metal–organic capsules through subcomponent self-assembly. Tetrahedra[7] and more complex prismatic structures,[7b,8] displaying facial (*fac*) and meridional (*mer*) coordination of ligands to octahedral metal centers, have been made by us through the assembly of various metal ions with linear dialdehydes and monoamines. However, so far the complementary diamine–monoaldehyde motif has afforded only tetrahedra.[9]

A new diamine ligand, 2,2′-bis(hydroxymethyl)benzidine (**1**), designed with the aim of preparing a cationic water-soluble tetrahedron, has displayed a versatile solubility, which allowed the exploration of self-assembly in various reaction media. This has enabled us to find experimental conditions that would favor *mer* over *fac* stereochemistry at the metal centers, thus increasing the structural complexity of the final assembly.[7b,8a]

Herein we report the preparation of an $Fe^{II}_4L_6$ tetrahedron, **2**, as well as a water-soluble $Fe^{II}_{10}L_{15}$ prism, **3**, from the same starting materials. Either **2** or **3** could be obtained by changing the reaction medium, and 4-methoxyaniline was observed to react selectively with **3** in the presence of **2**, thereby resulting in the complete disassembly of **3** to give mononuclear complex **4** and free **1** and **2** in solution.

The reaction of 2,2′-bis(hydroxymethyl)benzidine (**1**) (6 equiv) and 2-formylpyridine (12 equiv) in presence of $FeSO_4$ (4 equiv) in water at 50 °C led to the formation of $Fe^{II}_4L_6$ tetrahedron **2** (Scheme 1), which was characterized by NMR spectroscopy, ESI-MS spectrometry, elemental analysis, and X-ray crystallography (see the Supporting Information). Crystals of **2** as the hexafluorophosphate salt, $\mathbf{2}(PF_6)_8$, were obtained after anion metathesis and slow diffusion of diethyl ether into an acetonitrile solution of **2**.



Scheme 1. Preparation from subcomponents of tetrahedron **2** and prism **3** and their interconversion. Only one ligand is represented for clarity in each structure.

The tetrahedral assembly **2** has one bisbidentate bridging ligand (L) along each of the six edges of the Fe_4 tetrahedron (Figure 1). The metal centers in **2** have all *fac* arrangement of the coordinated ligands. The average metal-to-metal distance is 12.8 Å, similar to analogous tetrahedra.[9] The twelve CH_2OH groups on the periphery of **2** give water solubility to the assembly.

We were not able to grow crystals of **2** from its aqueous solution. Diffusion over one month of acetonitrile into an aqueous solution of **2** instead afforded single crystals[10] of the sulfate salt of **3**. The structure of **3** (Figure 2) can be seen as a twisted pentagonal prism, with each metal center defining a vertex. This prism is composed of two parallel staggered Fe_5L_5 pentagonal rings (Figure 2, depicted in orange), connected to each other at the iron(II) centers by five ligands (Figure 2, depicted in blue). The metal-to-metal distances range from 12.23 to 12.40 Å within the Fe_5L_5 rings and from 12.14 to 12.20 Å between pentagons. Whereas all iron(II)

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[*] S. Zarra, Dr. J. K. Clegg,[+] Dr. J. R. Nitschke
Department of Chemistry, University of Cambridge
Lensfield Road, Cambridge CB2 1EW (UK)
E-mail: jrn34@cam.ac.uk
Homepage: http://www-jrn.ch.cam.ac.uk/

[+] Current address: School of Chemistry and Molecular Biosciences
The University of Queensland
Brisbane St Lucia, QLD 4072 (Australia)

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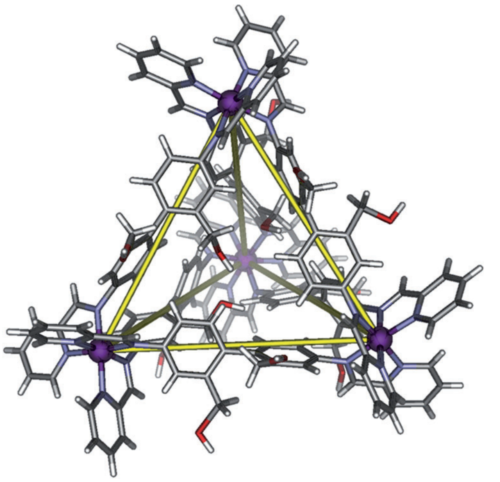


Figure 1. Crystal structure of **2**$(PF_6)_8$.[11] Disorder, anions, and solvent molecules are not shown for clarity. Connections between metal centers (purple spheres) are added to highlight the tetrahedral framework.

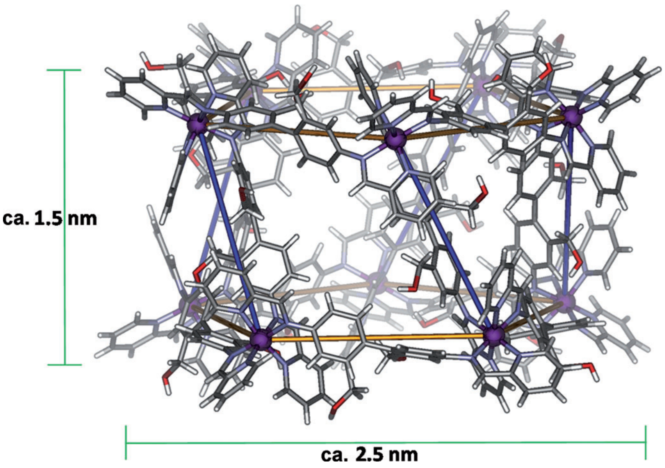


Figure 2. Crystal structure of **3**$(SO_4)_{10}$.[11] Disorder, anions, and solvent molecules are not shown for clarity. Connections between metal centers (purple spheres) are added to highlight the D_5-symmetric framework.

centers in **2** adopted *fac* stereochemistry, those in **3** had *mer*-arrangement. It is this change in stereochemistry at the metal centers that renders possible the formation of the new structure **3**.

We reported a series of pentagonal-prismatic architectures, $M^{II}_{10}L'_{15}$, having the same idealized D_5 point group symmetry as **3** (Figure 2). These were obtained through the reaction of different first-row transition metal ions, including Fe^{II}, with the same dialdehyde and monoamine.[7b,8b] Complex **3** shares with these structures an all-*mer* stereochemical configuration. However, owing to the different subcomponents employed in the syntheses, namely diamine and monoaldehyde for **3**, the average metal-to-metal distance in **3** (12.3 Å) is longer than that observed in the previously reported pentagonal-prismatic structures (8.3–8.6 Å). The increased ligand length in the present case results in a more open structure, thereby eliminating the well-defined guest binding pockets of the previous architectures. Moreover, the longer ligands give a greater twist of about 36° between the two parallel Fe_5 pentagons, thus approximating a regular pentagonal antiprism[12] (see Figure S13 in the Supporting Information). To our knowledge **3** is the first example of discrete complex to display a pentagonal-antiprismatic structure.[13] Another feature of **3** is its water solubility; this structure is the largest pyridylimine-based metal–organic complex to be soluble in this medium. Its dimensions were measured to be approximately 1.5 and 2.5 nm (Figure 2), and these make it one of the largest structures to be prepared by using subcomponent self-assembly.[8a,14]

The preparation of **3** from a solution of **2** by crystallization resulted in the isolation of **3** alone; the ^{1}H NMR spectrum of the bulk crystalline sample in D_2O can be assigned to only one species, **3**, having resonances at chemical shifts distinct from those of **2** (see Figure S17 in the Supporting Information). This observation suggests that **2** and **3** are in equilibrium in solution, with **3** preferentially crystallizing owing to its lower solubility, and eventually producing only **3**.[15] By ^{1}H NMR spectroscopy both **2** and **3** can be observed in the aqueous reaction mixture at 20 °C (ratio **2**/**3**, 80:20), whereas at 50 °C less than 2 % of **3** was observed.

Different concentrations, temperatures, and solvents were explored to selectively form **3** in solution (see Table S1 in the Supporting Information). It was observed that an increasing amount of methanol in the aqueous reaction mixture afforded a higher proportion of **3** after reaction at 20 °C for 20 h (see Figure S14 in the Supporting Information). A 50:50 (v/v) methanol/water mixture gave a **2**/**3** ratio of 50:50; whereas a 90:10 mixture allowed for the selective synthesis of **3** (Scheme 1).

As mentioned above, the ^{1}H NMR spectra of **2** and **3** were significantly different (see Figure S17). Provided that all metal centers within a single structure maintain the same Λ or Δ configuration, for tetrahedron **2** one would expect only one set of signals for each of the ligand's protons, because of its *fac* stereochemistry at the metal centers; whereas for **3** three sets of signals (ratio 1:1:1) are expected owing to the *mer* stereochemistry. These patterns of multiplicity are indeed observed in their ^{1}H–^{13}C HSQC NMR spectra (see Figures S6 and S11 in the Supporting Information). Moreover, the different stereochemistry at the metal centers for **2** and **3** is reflected in the red shift of the λ_{max} value of the metal-to-ligand charge-transfer absorption band in the UV/Vis spectra in going from *fac*-**2** to *mer*-**3**, as expected for low-spin d^6 metal ions[16] (see Figure S16 in the Supporting Information).

The ^{1}H NMR spectra of both **2** and **3** (see Figure S17) showed broad signals and displayed additional side bands around some major resonances, which we attributed to the presence of multiple axial conformers arising from hindered rotation about the central phenyl–phenyl bond of the biphenyl moieties.[17] This inference is further supported by the observation of chemical exchange cross-peaks between these resonances (see Figures S4 and S5 in the Supporting Information). The presence of H-bonding between the CH_2OH groups of each biphenyl ring is expected to contribute to the hindrance.[18] NMR spectra acquired at higher temperatures did not show appreciable coalescence of the signals as the temperature was increased within the accessible range (see Figure S7).

Diffusion ordered ^{1}H NMR spectroscopy (DOSY)[19] in D_2O solution confirmed the difference in size between tetrahedron **2** and pentagonal prism **3**, since their diffusion coefficients were found to be $(1.80 \pm 0.08) \times 10^{-10}$ and $(1.25 \pm 0.07) \times 10^{-10}\,m^2\,s^{-1}$, respectively. The ratio of their hydrodynamic volumes calculated through the Stokes–Einstein equation by assuming spherical shape for both structures[19] agreed fairly well with the volume ratio obtained by fully enclosing each of them in a sphere (see the Supporting Information).

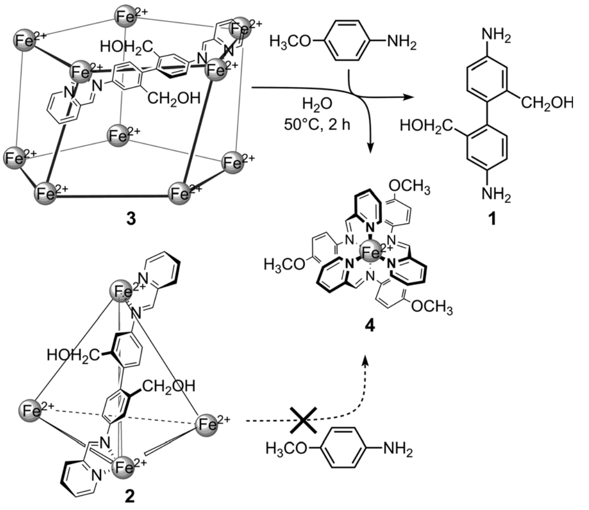
Prism **3** did not convert into tetrahedron **2** in solution in either water or methanol/water (90:10) during more than two months at room temperature. This suggests that **3** is kinetically trapped at this temperature owing to the cooperative locking effect[20] of 60 Fe^{II}–N bonds. Similar behavior has been observed in other structures involving more kinetically inert metals such as Pt^{II}[21] and Pd^{II}.[15a] Species with more labile metals, for example, Cd^{II} and Zn^{II}, have displayed lower stability in solution (conversion to smaller species in few weeks at room temperature and in hours at 60 °C).[15c]

Complete conversion of **3** to **2** could be achieved by heating a solution of **3** at 50 °C for one week in either water or methanol/water (90:10), thus indicating that the two structures are in an equilibrium that can be shifted depending on the conditions employed. Other experiments showed that the selectivity for the synthesis of **3** in methanol/water (90:10) decreased from > 95 % to 60 % in raising the temperature from 20 to 50 °C with a shorter reaction time (20 h). After one week **3** eventually converted into **2** (see Table S1 in the Supporting Information). These findings led us to infer that **3** is a kinetic product, and that **2** predominates at the thermodynamic equilibrium.

To further investigate their relative stabilities, a mixture of **2** and **3** (50:50 ratio) was allowed to react with 4-methoxyaniline. This amine has an electron-donating group in the *para* position, and we envisaged it would displace **1** in order to form the mononuclear complex **4**. Indeed, **3** was completely disassembled to form **4** and free **1** after 2 h at 50 °C (Scheme 2); however, **2** remained intact even after seven days in the presence of excess 4-methoxyaniline (20 equiv, see Figure S15 in the Supporting Information).

We recently reported a network of transformations based on cadmium(II) complexes, where it was possible to go sequentially from one structure to another upon application of appropriate stimuli;[8a] in the present system, however, we were able to convert only one of two architectures within a mixture into a new structure. Therefore these architectures displayed orthogonal reactivities[22] despite being composed of identical building blocks in the same ratios.

In conclusion, we have shown how the same mixture of starting materials can allow preparation of very different product structures, based in the present case upon the adoption of *fac* (**2**) versus *mer* (**3**) stereochemistry at the metal centers. A thorough investigation of the system enabled us to determine the conditions to selectively synthesize either one or the other, and to achieve their interconversion. Remarkably, the less stable structure **3** could be removed selectively from a mixture of **2** and **3** through conversion to the mononuclear species **4**. In similar systems, where the different structures effect different functions (tetrahedral capsules analogous to **2** have been observed to catalytically transform substrates,[1b] for example, and barrel-like structures similar to **3** might gate selected species through membranes[23]), these functions could be selectively deactivated through removal of one species from the system.



Scheme 2. Selective disassembly of **3** in presence of **2** to give the mononuclear complex **4** and free **1**. Complex **4** is represented only with *fac* stereochemistry, although a mixture of *fac* and *mer* complexes (15:85) was obtained in the reaction.

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