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COMMUNICATION

Self-assembly of a M_4L_6 complex with unexpected S_4 symmetry

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Using 1,4-diaminobenzene and 2-formylpyridine as simple building blocks results in a 1D ligand (rod, L2) to 2D (M_4L_4 grid, C1) to 3D (S_4 symmetrical M_4L_6 , C2) complexes upon sequential addition of Cu(I) and Fe(II) ions. The complex C2 can be seen as the smallest possible pseudo-tetrahedron with S_4 symmetry.

The growing demand for the understanding of the formation, structures and functionalities of self-assembled supramolecular structures, is one of the major challenges of supramolecular chemistry. One of the most recent developments in supramolecular chemistry¹⁻⁴ is the utilization of subcomponent self-assembly in which structures are generated *in situ* from their, often simple, subcomponents.⁵⁻⁷ This still immature field allows the construction of complex 3D structures⁸⁻¹¹ through spontaneous and hierarchical assembly by means of chemical reactions and weak intermolecular interactions. When one of the components are metal ions, the molecular architecture of these self-assembled 3D objects heavily depends on the nature of the coordination geometry of the metal ion used.¹²

The metal ion-assisted subcomponent self-assembly of an aromatic linear rigid bis-amine, 2-formylpyridine and Fe(II) ions resulting in a tetrahedral M_4L_6 cage in aqueous media reported by Nitschke and us opened a new page on molecular tetrahedral complexes.¹³ Later, the host-guest chemistry of the same tetrahedral cage was explored, demonstrating its potential as a container molecule for white phosphorus.¹⁴ Recently, we have expanded the same methodology to Co(II) and Ni(II) ions resulting in analogous tetrahedral M_4L_6 cage complexes with similar host-guest properties.¹² However, with structurally similar ligands the metal ions preferring tetrahedral coordination, such as Cu(I) and Ag(I), lead to the formation of molecular M_4L_4 grids.¹⁵ Combination of the rigidity and length of the ligands, the number of coordinating atoms of the *in situ* formed ligand and the coordination properties of the metal ion

(octa- or tetrahedral) governs the structure of the complex, *viz.* formation of either a tetrahedral M_4L_6 cage or a M_4L_4 grid.¹⁶

Following the subcomponent self-assembly approach, herein we demonstrate how a simple one dimensional (1D) rod-like ligand (L2) formed *in situ* from its subcomponents can selectively be transformed to either a two dimensional (2D) M_4L_4 grid¹⁵⁻¹⁸ or a three dimensional (3D) M_4L_6 tetrahedron¹⁹⁻²¹ (Fig. 1), depending on the metal ion used (Cu(I) or Fe(II)). In parallel, the preparation of M_4L_6 tetrahedron was also achieved via sequential self-assembly from 1D ligand through a 2D grid ending in a 3D complex by choosing an appropriate sequence²² of the metal ions.

In acetonitrile at 50 °C, when 1,4-diaminobenzene (1) and 2-formylpyridine (2) were mixed in a ratio of 1:2, an equilibrium mixture (Fig. 1) of 1, 2, L1 and L2 was observed. However, after addition of one equivalent of Cu(I), which prefers tetrahedral coordination, an already known M_4L_4 grid (C1) forms quantitatively.¹⁵ While previously L2 was first synthesized and converted to C1 upon complexation with Cu(I), we have used subcomponent self-assembly approach to drive the mixture of 1, 2 and Cu(I) ions to C1 (2D grid, Fig. 1). Finally, the grid C1 was further converted to a M_4L_6 complex with S_4 symmetry^{23, 24} (C2) using Fe(II) ions preferring octahedral coordination. This conversion is entropically favoured, because in total 11 components are switched into 14 components ($8 Fe^{2+} + 3 [Cu_4L_4]^{4+} \rightarrow 2 [Fe_4L_6]^{8+} + 12 Cu^+$). Interestingly, C2 can be seen as the smallest supramolecular M_4L_6 complex of its type reported to this date, possessing no internal cavity. The C2 was also obtained either by direct addition of Fe(II) to the L2 or mixing together 1, 2 and Fe(II) in a one pot reaction. The structure of C2 was established from NMR, X-ray crystallographic and ESI-MS analysis.

Fig. 1 represents the schematic models for the structures of $Cu_4(L2)_4$ grid (C1) and $Fe_4(L2)_6$ complex (C2). A M_4L_4 grid can be constructed from four 1D rods by joining their ends

through tetrahedrally coordinated vertices to form a square. This 2D grid structure can be further converted into a 3D M_4L_6 structure by diagonally connecting the pairs of opposite vertices of the square grid from the top as well as from the bottom via octahedrally coordinated vertices (Fig. 1.).

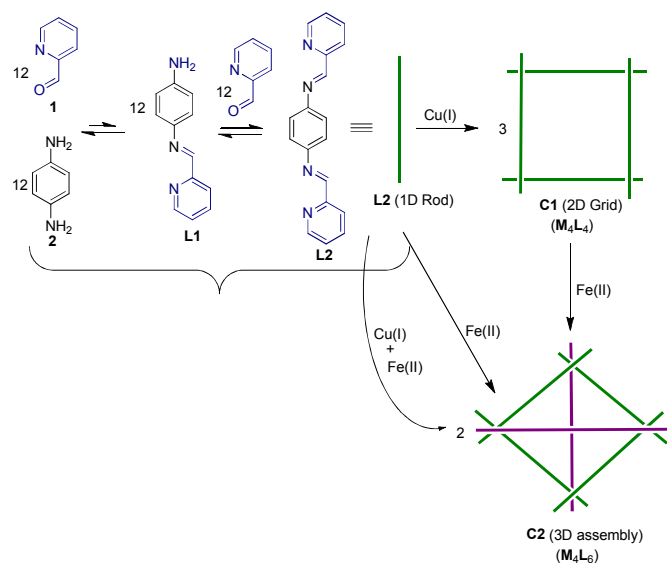


Fig. 1 Cartoon representation of the formation of M_4L_6 complex (**C2**) via 2D grid (**C1**) and/or 1D rod (**L2**).

The NMR spectra could be fully assigned to establish the relative composition of the components during the reaction. The 1H NMR spectra analysis indicated that the components **1**, **2**, **L1** and **L2** were present in a ratio of 4:0:2:3 before addition of $Cu(I)$. However, after the addition of $Cu(I)$, only **C1** is observed (Fig. S7, ESI⁺). The 1H NMR spectrum of the tetrahedral complex **C2** (M_4L_6) is shown in Fig. 2. The chemical shifts of the protons of **L2** (1D rod), e.g. H_a - H_d (aromatic), H_e (iminic proton) experience down-field shift (12.26-10.90 ppm). In addition, three different kinds of signals for the H_e , H_f - H_g (phenyl moiety, Fig. 2) clearly indicate that **L2** experiences three different magnetic environments in the complex **C2**. This observation was further supported by single crystal X-ray analysis (*vide infra*).

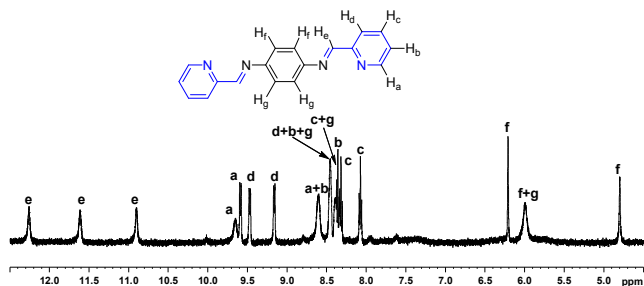


Fig. 2 1H NMR spectra of complex **C2** in acetonitrile, full range was not shown for the clarity.

The crystal structure of **C1** has already been reported in the literature.¹⁵ Slow diffusion of diisopropyl ether into an acetonitrile solution of **C2** yielded moderate quality single crystals on which X-ray structural analysis was performed. The detailed analysis of the crystal structure of **C2** shows that it does not possess a true tetrahedral (T) symmetry (Fig. 3). Since the asymmetric unit contains one whole $Fe_4(L_2)_6$ complex, its symmetry in the crystal structure is C_1 rather than S_4 , however, with only minor deviations in the actual geometry, thus suggesting the higher S_4 symmetry in solution. Still, the crystal structure shows that the **C2** contains two clearly different sets of ligands. Four out of the total six ligands are configurationally very similar, *viz.* they are nearly planar so that the torsion angles [defined as $N(\text{pyr})-Fe-Fe-N(\text{pyr})$] between the coordinating pyridyl moieties are close to zero ($1-10^\circ$) and that the central phenyl ring is twisted ca. 45° with respect to the mean plane of the pyridyl rings (Fig. 3, the ligands labelled in green), displaying a *syn*-configuration. The remaining two ligands are much more twisted, the corresponding torsion angles being ca. 135° between the pyridyl rings and the central benzene ring twist of ca. 67° (Fig. 3, the ligands labelled in purple), thus being in *anti*-configuration. In **C2**, the $Fe(II)$ centres are not equidistant, yet are very close to being so, with the distances varying between 8.47 and 8.53 Å.

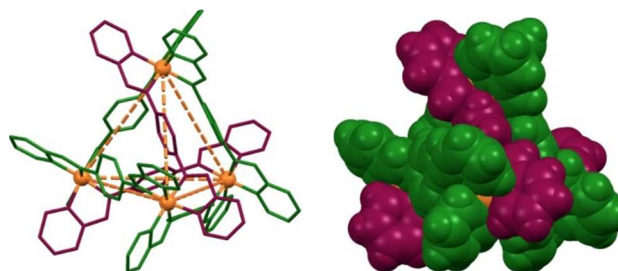


Fig. 3 The X-ray structure of the complex **C2**: stick model (left) and space filling model (right) are shown.

The four *syn*-configured ligands can be seen to originate from a $Fe_4(L_2)_4$ grid which is then diagonally capped with the two *anti*-configured ligands. The *anti*-ligands (purple in Fig. 3) are at a 90° angle with respect to each other and occupy the clefts created by pairs of the *syn*-ligands. Indeed, omitting the *anti*-ligands (purple in Fig. 3) from the structure of the $Fe_4(L_2)_6$ complex, an extremely twisted grid-like $Fe_4(L_2)_4$ structural framework is exposed. Closer inspection of this M_4L_4 substructure reveals that it is a 90° -twisted molecular grid (green ligands in Fig. 3). The capping of the $Fe_4(L_2)_4$ grid substructure by two *anti*-ligands leads to an S_4 -symmetric assembly implying a $\Delta \Delta \Delta \Delta$ configuration of the Fe centers.²³ Interestingly, no diastereomers of the $Fe_4(L_2)_6$ complex other than the S_4 one were detected either by X-ray or 1H NMR analysis. Thus, due to the differences in configurations of the **L2** ligands, the $Fe_4(L_2)_6$ complex can be defined as a twisted

grid capped with two auxiliary ligands, *viz.* (*anti-L2*)₂Fe₄(*syn-L2*)₄ rather than as a tetrahedral Fe₄(L2)₆.

The very short and rigid central part of the L2 ligand leads to very close packing of the ligands in the Fe₄(L2)₆ and the two hydrogen atoms of the two *anti*-ligands point to the center of the complex (in tetrahedral fashion), leaving no cavity for host-guest chemistry.⁶ Using other rigid aromatic diamines as the central part of the ligands leads to tetrahedral complexes with cavities ranging from about 130 to 800 Å with the notable exception of the recent work by Nitschke with 2,6-diamino-substituted naphthalene-, anthracene- or anthraquinone-based S₄-configured cages which have no or very small (< 20 Å³) cavities.²³

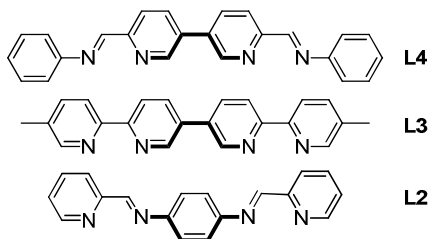


Fig. 4 Ligands L2, L3 and L4.

The choice of the shortest linear rigid diamine (1,4-diaminobenzene) was guided by the idea to explore the influence of steric and coordination geometry constraints of the *in situ* formed ligands and the metal ions used on the formation of the presumably smallest possible M₄L₆ complex of its kind. The ligands L3²⁵ and L4²⁶ (Fig. 4) which are structurally similar to L2 resulted in M₄L₆ complexes of different stereochemistry, ΔΔΔΔ or ΛΛΛΛ, compared to C2, which exhibits ΔΔΔΔ configuration of metal vertices. Furthermore, the distances between the Fe(II) metal centres differ significantly between complex with L2 and those with L3 and L4, with the X-ray structures revealing Fe-Fe distances of 9.44–9.50 Å for L3 complex and 9.24–9.60 Å for L4 complex, while the Fe-Fe distances in C2 are significantly shorter (8.47–8.53 Å). While this might seem as somewhat unexpected, given that the two coordinating moieties (2-pyridylimino or 2,2'-bipyridyl) in all three ligands are separated by four sp² carbons, there are two crucial differences between L2 and L3/L4 causing such behaviour. First, the distance between the coordinating moieties is fixed in L2, while the 3,3'-bipyridyl core in L3/L4 offers some conformational flexibility by means of relatively unhindered rotation around the single bond between the pyridyl rings. This also means that the steric bulk of the spacer is located in the center of the ligand in case of L2, while being shifted to the ligand periphery in L3/L4. We believe these two effects result in reduced Fe-Fe distance and tight packing of the ligands, leading to a purely S₄-symmetrical assembly and leaving no space for potential guest inclusion.

In conclusion, the subcomponent self-assembly methodology was used to make, to the best of our knowledge, the smallest reported supramolecular M₄L₆ S₄-symmetrical

pseudo-tetrahedral complex with ΔΔΔΔ-configuration of its vertices. Due to the small size of the ligands and their tight packing, the Fe₄(L2)₆ complex does not have an internal cavity to accommodate any guest molecules. We are currently focusing our interest towards development of unpredictable assemblies and conformational changes from simple building blocks by using kinetic and thermodynamic effect for different diamines.²⁷

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Notes and references

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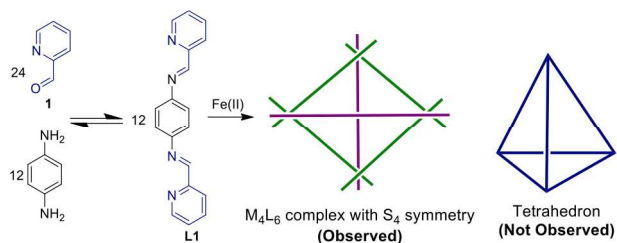
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†Electronic Supplementary Information (ESI) available: [Experimental details, NMR and MS spectra and X-ray single crystal structure analysis (CCDC 1002402)]. See DOI: 10.1039/b000000x/.

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Table of Contents Synopsis and Graphic



In one-pot subcomponent reaction 1,4-diaminobenzene and 2-formylpyridine, as the reacting components, self-assemble to a small supramolecular M₄L₆ tetrahedron with unexpected S₄ symmetry in presence of Fe(II) ions.