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## Self-Assembly of a Metallomacrocyclic Templated by Iron(II)

Feng Li, Jack K. Clegg, David Price, and Cameron J. Kepert\*

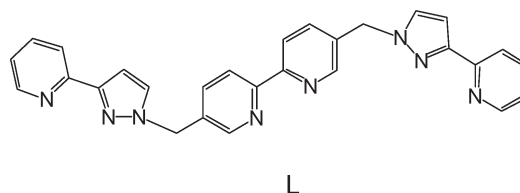
*School of Chemistry, University of Sydney, New South Wales 2006, Australia*

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An unusual discrete heteronuclear metallomacrocyclic was designed and synthesized via metal-ion-directed self-assembly by an iron(II) template. The formation of this metallomacrocyclic was demonstrated by X-ray crystallography, electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry, and NMR spectroscopy.

Supramolecular architectures formed by metal-ion-directed self-assembly have received considerable attention because of their intriguing geometries including helicates,<sup>1</sup> cages,<sup>2</sup> rotaxanes, catenanes, and knots,<sup>3</sup> and their diverse potential applications in host–guest chemistry, magnetism, electrochemistry, optics, and catalysis.<sup>1a–c,e,3b,3g,3i</sup> Despite many advances in the field, including the development of

different strategies such as subcomponent self-assembly,<sup>4,5</sup> secondary building unit,<sup>6</sup> and hierarchical self-assembly<sup>7</sup> strategies, the rational control of the structure of multi-component assemblies, particularly those containing more than one metal ion,<sup>8</sup> still remains a significant challenge for the supramolecular chemist. The rational design of suitable organic ligands and the judicious choice of metal ions play important roles in the construction of these species. Here we report the synthesis of an iron(II)-templated self-assembly of an Ag<sub>3</sub>FeL<sub>3</sub> metallomacrocyclic based on a multidentate nitrogen-donor ligand **L** with three coordinating moieties.



\*To whom correspondence should be addressed. E-mail: c.kepert@chem.usyd.edu.au.

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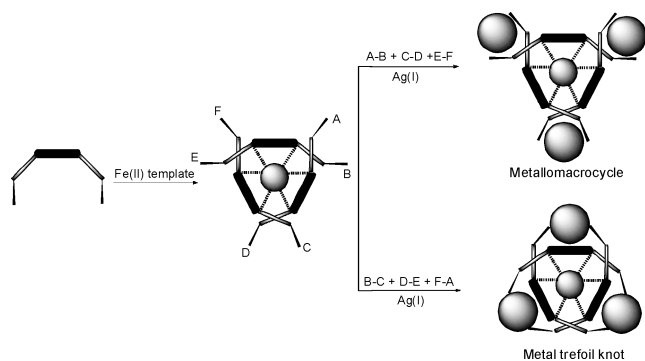
The use of a tris-chelated octahedral metal ion to template supramolecular assemblies of interesting topology has been done a number of times, particularly in the synthesis of catenanes and knots. Such an approach was first proposed for the assembly of a covalently linked trefoil knot in 1973 by Sokolov,<sup>9</sup> and Hunter et al. recently reported the synthesis of such a species using a zinc(II) ion template.<sup>3h</sup> In focusing on a coordinatively linked approach, we hypothesized, by analogy with numerous catenane systems, that the presence of a short spacer length between donor moieties of **L**, that is, the methylene spacers between bipyridine (bpy) and polypyrazole units, should favor the formation of a macrocyclic species (Scheme 1), while a longer spacer (as is present in

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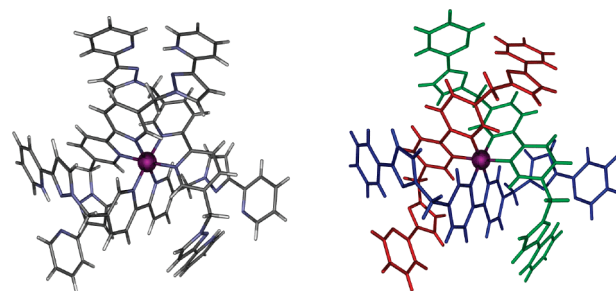
**Scheme 1.** Schematic Representation of the Synthesis of a Metallomacrocyclic or a Metal Trefoil Knot by an Octahedral  $[\text{Fe}(\text{bpy})_3]^{2+}$  Template



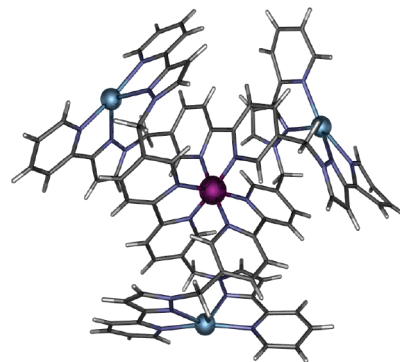
the examples cited above) would favor the formation of a trefoil knot.<sup>10</sup>

The ligand **L** was prepared by the reaction of 3-(2-pyridyl)pyrazole with 5,5'-bis(bromomethyl)-2,2'-bipyridine under basic conditions<sup>11</sup> (the synthesis and characterization of ligand **L**, including its X-ray structure, are given in Figure S1 in the Supporting Information, SI). The reaction of ligand **L** with  $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in  $\text{CH}_3\text{CN}$  gives rise to a clear-red solution. The electrospray ionization Fourier transform ion cyclotron resonance (ESI-FTICR) mass spectrum (Figure S4 in the SI) of this solution shows peaks at  $m/z$  733.26 ( $[\text{FeL}_3]^{2+}$ ) and 1566.51 ( $[\text{FeL}_3](\text{ClO}_4)^+$ ). The appropriate isotope patterns for their charged states (Figure S5b,c in the SI) were observed, indicating a mononuclear tris(bipyridine) complex. The electronic absorption spectrum shows bands at 523 nm ( $[\text{FeL}_3](\text{ClO}_4)_2$ ) and 525 nm ( $[\text{FeL}_3](\text{BF}_4)_2$ ) in the visible range, which correspond to the metal-to-ligand charge-transfer (MLCT) bands of an  $\text{Fe}(\text{bpy})$  unit.<sup>12</sup> These observations are in agreement with the complexation of three bpy units by each iron(II) center. NMR spectra of the complex indicated the formation of a highly symmetric species that could be fully assigned (see the SI), with the proton signals assigned to the bpy moiety shifted upfield relative to the free ligand. In addition, the signals of the  $-\text{CH}_2-$  groups of the bridges between the bpy and pyridylpyrazole units appear as a singlet in the free ligand and as a pair of doublets in the complex. Formation of the tris-chelate iron(II) complex is confirmed from the single-crystal X-ray structure of  $[\text{Fe}(\text{LH})_3](\text{BF}_4)_5 \cdot 3.25(\text{MeNO}_2) \cdot 3.25\text{H}_2\text{O}$  (Figure 1), where the crystals were formed upon slow diffusion of diethyl ether vapor into a solution of the complex in  $\text{MeNO}_2$ . The compound crystallizes in the nonchiral space group  $P\bar{1}$ , with both enantiomers ( $\Delta$  and  $\Lambda$ ) of the cation present within the lattice. The central iron(II) ion has a distorted octahedral coordination sphere surrounded by six nitrogen atoms of the three twisted ligands. The six terminal pyridylpyrazole units are brought into close proximity via hydrogen bonding and appear to be ideally preorganized for complexation with an additional metal ion to link the pyridylpyrazole units of adjacent ligands and form a metallomacrocyclic structure rather than a trefoil knot.

Therefore, 3 equiv of  $\text{AgClO}_4$  was added to a solution of  $[\text{FeL}_3](\text{ClO}_4)_2$  in  $\text{CH}_3\text{CN}$ , resulting in the formation of  $[\text{Ag}_3\text{FeL}_3](\text{ClO}_4)_5$ . The resulting complex was investigated by 1D



**Figure 1.** Complex cation in the crystal structure of  $[\text{Fe}(\text{LH})_3](\text{BF}_4)_5 \cdot 3.25(\text{MeNO}_2) \cdot 3.25\text{H}_2\text{O}$ .



**Figure 2.** Structure of the metallomacrocyclic cation  $[\text{Ag}_3\text{FeL}_3]^{5+}$ . The solvent of crystallization, regions of disorder anions, and coordinated water molecule are omitted for clarity.

and 2D NMR spectroscopy ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^1\text{H}-^1\text{H}$  COSY), yielding highly symmetric spectra (see the SI). All peaks attributed to the aromatic protons were assigned by H-H COSY experiments. When compared to the spectrum of  $[\text{FeL}_3](\text{ClO}_4)_2$ , there are significant shifts in the peaks attributed to the methylene protons and also significant downfield shifts attributable to those of the pyridylpyrazole units (see Figure S2 in the SI), consistent with complexation to silver(I). ESI-FTICR mass spectra confirmed that the species had a stoichiometry of  $[\text{Ag}_3\text{FeL}_3](\text{ClO}_4)_5$ . Ultimate proof of the formation of the  $\text{Ag}_3\text{FeL}_3$  metallomacrocyclic species was obtained via X-ray diffraction. When excess  $\text{KPF}_6$  was added to an acetonitrile/ethanol solution of  $[\text{Ag}_3\text{FeL}_3](\text{ClO}_4)_5$  followed by slow evaporation, pink needles suitable for diffraction studies could be isolated. Structural analysis (Figure 2) reveals a formula of  $[\text{Ag}_3\text{FeL}_3 \cdot \text{OH}_2](\text{ClO}_4)(\text{PF}_6)_4 \cdot \text{EtOH}$  in which the iron(II) remains complexed in an octahedral geometry to the bpy units, while the pyridylpyrazole units coordinate to the silver ions. The arrangement of the ligands is almost identical with that in the structure of  $[\text{Fe}(\text{LH})_3](\text{BF}_4)_5 \cdot 3.25(\text{MeNO}_2) \cdot 3.25\text{H}_2\text{O}$  described above, with the hydrogen-bonding motif substituted for the silver ions. Within the crystal structure, the metallomacrocyclics link through argentophilic interactions  $[\text{Ag}(1) \cdots \text{Ag}(1) = 3.377(5) \text{ \AA}; \text{Ag}(2) \cdots \text{Ag}(2) = 3.18(2) \text{ \AA}]$  to form chiral 1D chains that contain solely the  $\Delta$  or  $\Lambda$  forms of the complex; these alternate in chirality throughout the centrosymmetric structure (space group  $Pbcn$ ). The third silver atom, rather than form a further linkage, coordinates to a water molecule  $[\text{Ag}(3)-\text{O}(1\text{W}) = 2.56(3) \text{ \AA}]$ .

In conclusion, an unusual heteronuclear metallomacrocyclic has been rationally designed and synthesized through an octahedral iron(II) template. The formation of this

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coordinatively linked moiety was unambiguously demonstrated by X-ray crystallography in the solid state and ESI-FTICR mass spectrometry and NMR spectroscopy in solution. This synthetic strategy may open broad interest in the construction of new interlocking ring topologies. Further work on the self-assembly of metallosupramolecular architectures by this synthetic strategy using extended ligands is in progress.

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**Supporting Information Available:** Experimental details for the synthesis of ligand **L** and metal complexes  $[\text{FeL}_3](\text{ClO}_4)_2$ ,  $[\text{FeL}_3](\text{BF}_4)_2$ ,  $[\text{Ag}_3\text{FeL}_3](\text{ClO}_4)_5$ , and  $[\text{Ag}_3\text{FeL}_3](\text{ClO}_4)(\text{PF}_6)_4$ , NMR and ESI-MS spectra of the reported compounds, molecular structures of **L**,  $[\text{Fe}(\text{LH})_3](\text{BF}_4)_5 \cdot 3.25(\text{MeNO}_2) \cdot 3.25\text{H}_2\text{O}$ , and  $[\text{Ag}_3\text{FeL}_3 \cdot \text{OH}_2](\text{ClO}_4)(\text{PF}_6)_4 \cdot \text{EtOH}$ , single-crystal X-ray data, and a CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.