

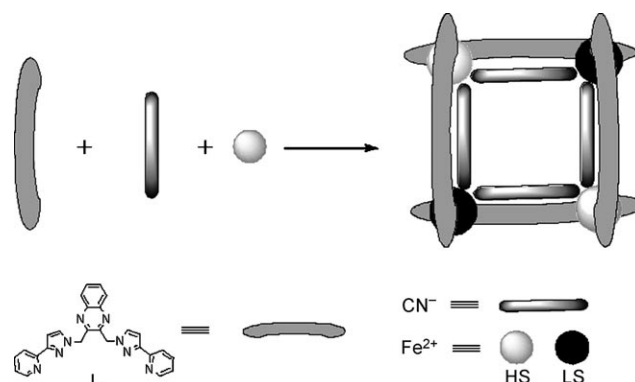
A Mixed-Spin Molecular Square with a Hybrid [2 × 2]Grid/Metallocyclic Architecture**

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The design and synthesis of molecular architectures displaying a range of tunable and potentially useful properties has been the subject of widespread attention over the past decade.^[1] Both discrete and polymeric metallosupramolecular assemblies have been shown to exhibit intriguing properties, with potential applications including gas separation and adsorption,^[2] catalysis,^[3] photoactivity,^[4] magnetism,^[5] electrochemistry,^[4a] and host–guest behavior.^[4c,6] Cyanide-bridged metal–organic framework materials have attracted intense research interest for their magnetic properties; for example, Prussian Blue is known to be a molecule-based magnet with a Curie temperature (T_c) of 5.6 K, while some heterometallic analogues have been shown to function as high T_c magnets with ordering temperatures up to 372 K.^[7] Metallo-cycles and grids represent comparatively simple systems in which the tunability of the molecular structure and ensuing physico-chemical properties can be explored. Although a number of grids and metallocycles displaying interesting magnetic and spin-crossover properties have been developed,^[5b,8] the design and successful construction of these systems, particularly those exhibiting multiple spins at room temperature, still represents a significant challenge.^[9] Herein we report the synthesis and characterization, and the magnetic and electronic properties, of a mixed-spin Fe_4 -molecular square with a hybrid grid/metallocyclic architecture.

Based upon the decomposition of selenocyanate, we now report a rare example of a hybrid grid/metallocyclic architecture containing both **L** (2,3-bis[3-(pyridin-2-yl)-1*H*-pyrazol-1-yl]methyl]quinoxaline) and cyanide-bridged Fe^{II} (high-spin, HS)– Fe^{II} (low-spin, LS) molecular square at room

temperature, which has been constructed through a metal-directed self-assembly strategy (Scheme 1).



Scheme 1. Synthesis of the hybrid-[2×2]grid/metallo-macrocycle by metal-directed assembly based upon the decomposition of selenocyanate.

The ligand **L** was prepared according to the previously published methodologies.^[10] The reaction of $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, KSeCN , and ligand **L** in a mixture of CH_3CN and CH_3OH resulted in a yellow solution, from which single red crystals were formed upon slow diffusion of diethyl ether in 88% yield. In the electrospray-ionization Fourier transform ion cyclotron resonance (ESI-FTICR) mass spectrum (Supporting Information, Figure S1), the major peak is observed at m/z 1158.16 [$[\text{Fe}_4(\text{CN})_4\text{L}_4](\text{SeCN})_2]^{2+}$], which is consistent with the loss of two anions from the tetranuclear square. Several minor fragments were also identified; for example, the loss of four anions [$[\text{Fe}_4(\text{CN})_4\text{L}_4]^{4+}$] at m/z 526.12, three anions [$[\text{Fe}_4(\text{CN})_4\text{L}_4](\text{SeCN})]^{3+}$] at m/z 737.13, and one anion [$[\text{Fe}_4(\text{CN})_4\text{L}_4](\text{SeCN})_3]^{+}$] at m/z 2421.29. The appropriate isotope patterns for their charged states (Figure S1b and c) were observed, thus indicating the presence of a tetranuclear iron(II) complex. The solid state UV/Vis/NIR spectrum of the molecular square over the region 2000–200 nm (Figure S2) revealed a relatively low absorption band at 905 nm (11075 cm^{-1}) and an intense band at 425 nm (23475 cm^{-1}). The latter is attributed to a metal-to-ligand (MLCT) ($d\text{--}\pi^*$) transition characteristic of an Fe^{II} center coordinated to a pyridyl-based ligand such as **L**.^[9a] The relatively low intensity band at 905 cm^{-1} is likely to arise from Laporte or spin-forbidden $d\text{--}d$ transitions which are localized at the HS Fe^{II} centers.

The formation of the complex $[\text{Fe}_4(\mu\text{-CN})_4\text{L}_4](\text{CN})_2(\text{SeCN})_2 \cdot 4\text{H}_2\text{O}$ was determined by single-crystal X-ray dif-

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Supporting information for this article (additional experimental details of the X-ray and magnetic and mass spectral determinations) is available on the WWW under <http://dx.doi.org/10.1002/anie.201007409>.

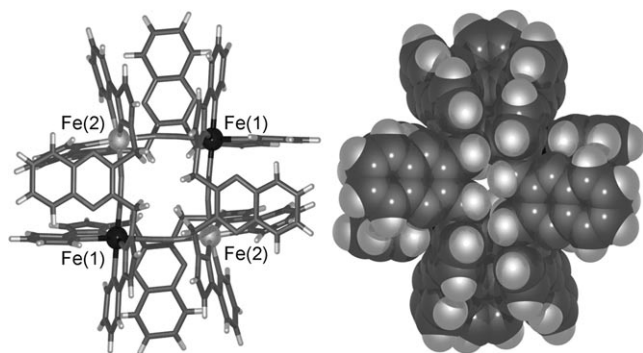


Figure 1. Structure of the tetranuclear cation $[\text{Fe}_4(\text{CN})_4\text{L}_4]^{4+}$. Left: overall view of the molecule. Black and gray spheres represent the low-spin and high-spin Fe^{II} centers, respectively. Right: space-filling model of the hybrid $[2 \times 2]$ grid/metallomacrocyclic. Solvent molecules and counter ions are omitted for clarity.

fraction (Figure 1). The hybrid grid/metallomacrocyclic crystallizes in the orthorhombic space group $Fdd2$ with $1/2$ a molecule per asymmetric unit. The four octahedral Fe^{II} centers are bridged by the bis-bidentate ligands in a $[2 \times 2]$ grid-like arrangement. Adjacent iron centers are also bridged by *cis*-orientated cyanide ligands forming a square metalocycle with approximately $5.12 \text{ \AA}$ between metal centers. Each complex is chiral, with either $\Delta\Delta\Delta\Delta$ or $\Lambda\Lambda\Lambda\Lambda$ configurations at the metal centers. The two iron environments exist in different spin states. Fe(1) has a C_2N_4 coordination environment with average bond lengths of $2.05 \text{ \AA}$ suggesting it is principally low-spin, while Fe(2) has an N_6 coordination environment with longer bonds at $2.12 \text{ \AA}$ suggesting it is principally high-spin; normally, a approximately $0.2 \text{ \AA}$ difference would be expected between these values, and we attribute the smaller differential to the presence of some degree of static disorder of the square in which the cyanido linkages are inverted.

The magnetic properties of the complex have been measured (Figure 2). The magnetic susceptibility ($\chi_M T$) of $7.44 \text{ cm}^3 \text{ K mol}^{-1}$ at room temperature indicates the presence of two Fe^{II} ions in a HS state ($g = 2.22$, $S = 2$) and two Fe^{II} ions in a LS state ($S = 0$), thus confirming the mixed-spin state of

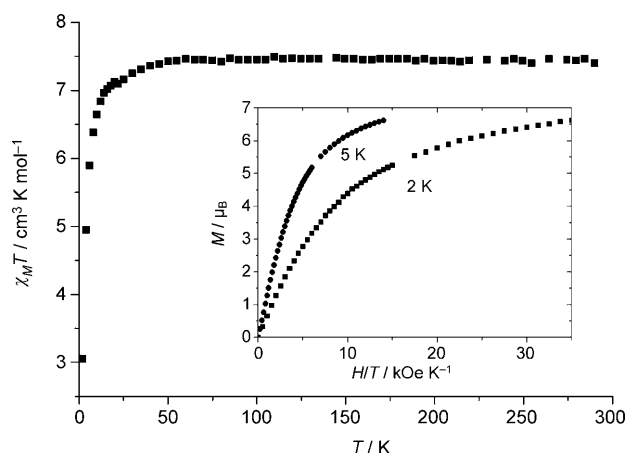


Figure 2. Temperature dependence of the magnetic susceptibility ($\chi_M T$). The inset shows the reduced magnetization curves at 2 and 5 K.

the complex. The decrease in $\chi_M T$ below 50 K may be attributed to zero-field splitting (ZFS) for Fe^{II} , and possibly also to the presence of weak antiferromagnetic exchange between the HS Fe^{II} centers. The inset in Figure 2 shows that the reduced magnetization curves (M vs H/T) do not display any saturation up to 7 T and are not superimposable. These factors indicate the presence of magnetic anisotropy due to ZFS. In addition, since antiferromagnetic interactions between $\text{Fe}^{\text{II}}_{\text{HS}}$ would be mediated by the $[\text{Fe}^{\text{II}}_{\text{LS}}(\text{CN})_2(\text{L})_2]$ diamagnetic moieties, they are expected to be very weak.

Similar magnetic behavior has been reported for the two square grid structures $[\text{Fe}_4(\mu\text{-CN})_4(\text{phen})_4\{(\text{6-methylpyrid-2-ylmethyl})\text{bis}(\text{pyrid-2-ylmethyl})\text{amine}\}_2](\text{PF}_6)_4$ and $[\text{Fe}_4(\mu\text{-CN})_4(\text{phen})_4\{(\text{bis}(\text{6-methylpyrid-2-ylmethyl})\text{pyrid-2-ylmethyl})\text{amine}\}_2](\text{PF}_6)_4$ (phen = 1,10-phenanthroline).^[9f] These structures exhibit two different Fe^{II} coordination environments, N_6 and N_4C_2 , respectively, in the HS and LS states from 4 to 300 K. The cyanide carbon atoms act as π acceptors^[11] thus giving rise to a strong ligand field such that the Fe^{II} ions in an N_4C_2 environment are generally in the LS state.

Cyclic voltammetry of the complex in 0.1 M $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{PF}_6/\text{CH}_3\text{CN}$ electrolyte revealed four successive one-electron redox processes in the region 0.5–2.0 V (vs ferrocene/ferrocenium) on the forward potential sweep from 0–2.0 V (Figure 3). Only two redox processes are discernible

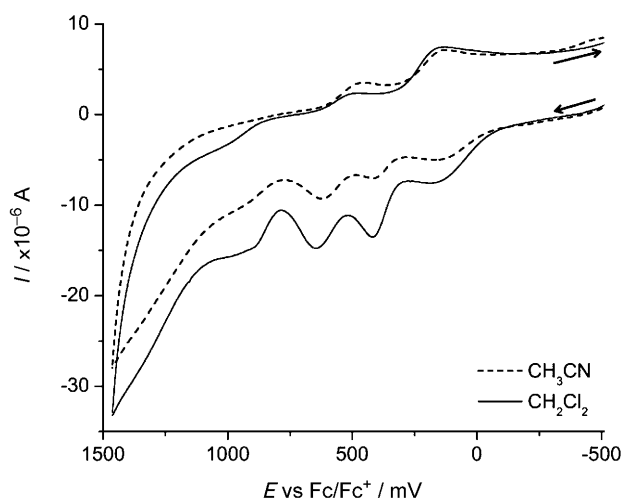


Figure 3. CV data for the complex in 0.1 M $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{PF}_6/\text{CH}_3\text{CN}$ and CH_2Cl_2 electrolytes.

in the reverse potential scan suggesting that decomposition of the molecular square occurs following oxidation of the Fe^{II} centers to Fe^{III} . It is reasonable to assign the first two processes to the oxidation of the high-spin N-bound centers, followed by the oxidation of the low-spin C-bound centers, in accord with previous literature reports of cyanide-bridged iron, cobalt, and ruthenium molecular squares.^[9a,b,12] The use of the non-coordinating solvent CH_2Cl_2 instead of CH_3CN revealed similar electrochemical behavior for the complex in the forward potential scan; however, three redox processes were discernible in the reverse scan. In both electrolytes, the

redox processes are altered significantly during the repeat CV scan, suggesting that decomposition of the complex occurs in both solvents; however, the lack of the inherent stability of the supramolecular motif, rather than the coordinating ability of the solvent, drives the decomposition process. The cathodic region of the CV did not exhibit any discernable redox processes.

The evidence of a splitting between the redox processes for the four iron centers suggests that the metals are weakly coupled through the ligand backbone. In molecular squares bridged solely by cyanide ligands, two two-electron redox processes are observed due to successive oxidation of the two N-bound and two C-bound Fe centers.^[9a] In the present case, however, both the cyanide bridge and the carbon backbone of **L** link the adjacent Fe^{II} centers, which provides for electronic communication, albeit weak, between the adjacent ions.

In conclusion, we have described a straightforward strategy for the in situ ligand synthesis of a novel cyanide-bridged metallomacrocyclic [Fe₄(μ-CN)₄L₄]⁺, which has been structurally characterized by X-ray crystallography. Magnetic measurements indicate the presence of both high-spin and low-spin Fe^{II} centers, while the electrochemical data are consistent with weak electronic coupling between the adjacent metal ions. Further studies are underway to elaborate the metal ions that are amenable to this synthetic strategy.

Experimental Section

[Fe₄(μ-CN)₄L₄](CN)₂(SeCN)₂·4H₂O: A 500 mg quantity (1.13 mmol) of ligand **L** was dissolved in 150 mL of CH₃CN. A second solution, containing 388 mg (1.15 mmol) of Fe(BF₄)₂·6H₂O and 334 mg (2.32 mmol) of KSeCN in 15 mL of MeOH was prepared and left stirring for 30 min. This solution was added dropwise. The reaction mixture was heated to reflux overnight. The mixture was then cooled to room temperature and filtered. Slow diffusion of diethyl ether into the filtrate resulted in the formation of red crystals of [Fe₄(μ-CN)₄L₄](CN)₂(SeCN)₂·4H₂O. Yield: 88%. ESI-HRMS (positive-ion detection, CH₃CN): *m/z* 1158.16085 (calcd 1158.15740 for [(Fe₄(CN)₄L₄)(SeCN)₂]²⁺). IR (KBr), $\tilde{\nu}_{\text{max}}$ [cm⁻¹]: 3371w, 3118m, 2081s (CN), 1438m, 1253m, 1073m, 768s. UV/Vis/NIR (solid state), λ_{max} [nm]: 905, 425. Single crystals taken from the same sample and used directly in the X-ray study were found to correspond to a formula of [Fe₄(μ-CN)₄L₄](CN)₂(SeCN)₂·4H₂O.

CCDC 791478 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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