

Magneto-Structural Correlations in Self-Assembled Spin-Transition Nano-Architectures of the $[\text{Fe}_4^{\text{II}}\text{L}_4]^{n+}$ $[2 \times 2]$ -Grid-Type

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Abstract

The magnetism of a series of tetranuclear complexes of the $[\text{Fe}_4^{\text{II}}\text{L}_4](\text{BF}_4)_n$ $[2 \times 2]$ -grid-type was investigated, revealing the occurrence of spin transition behavior within this class of compounds. The phenomenon depends directly on the nature of the substituent R^1 of the ligand L . All Fe^{II} ions in compounds with R^1 substituents favoring strong ligand fields ($\text{R}^1 = \text{H}; \text{OH}$) remain completely in the diamagnetic low spin state. Only the complex bearing $\text{R}^1 = \text{Ph}$ exhibits thermally induced spin transition behavior. © 2001 Elsevier Science. All rights reserved

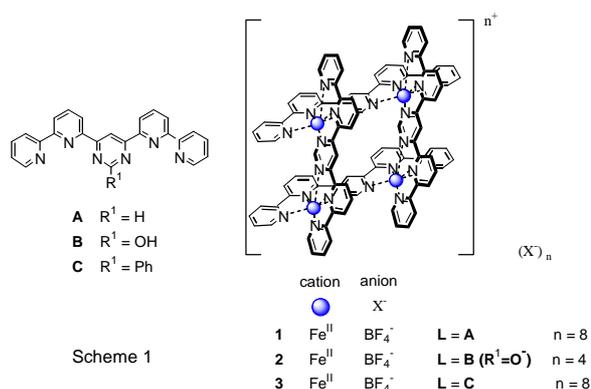
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Among the accessible physical effects, the spin transition (ST) phenomenon of Fe^{II} ions is one of the perspective processes to enable molecular memory effects due to the concomitance of possible “write” (temperature, pressure, light) and “read” (magnetic, optical) parameters. [1]

In a previous communication, a $[2 \times 2]$ grid-type Fe_4^{II} complex (**1** herein) has been described as the first tetranuclear compound exhibiting ST properties, generated by a consequent application of self-assembly on ST-systems. [2]

Since self-assembled tetranuclear $[\text{Fe}_4^{\text{II}}\text{L}_4]^{n+}$ $[2 \times 2]$ grid type species appeared to be a promising new class of ST compounds, a series of complexes $[\text{Fe}_4^{\text{II}}\text{L}_4](\text{BF}_4)_n$ **1–3** ($\text{L} = \text{A}$, $n=8$; B , $n=4$; and C , $n=8$) was synthesized and their magnetic properties were studied both in solution and in the solid state. Within the series of compounds **1–3** $[\text{Fe}_4^{\text{II}}\text{L}_4](\text{BF}_4)_n$, the coordination sphere and so the strength of the ligand field of the Fe^{II} ions was varied by changing the substituent R^1 in the 2-position of the pyrimidine of the incorporated ligands L ($\text{L} = \text{A}$, B , and C with $\text{R}^1 = \text{H}$, O^- , and Ph ; Scheme 1).



First evidence for a different magnetic behavior of the incorporated Fe^{II} ions in compounds **1–3** was found in the room temperature $^1\text{H-NMR}$ spectra: complexes **1** and **2** exhibit only signals in the region expected for diamagnetic Fe^{II} low spin (LS) complexes ($\delta = 0$ to 10 ppm). In contrast, complex **3** shows peaks spread across a wide range ($\delta = -20$ to 80 ppm) indicating the presence of paramagnetic species

(Figure 1). This strong shift of peaks in the proton NMR spectra is caused by the high local field typical for incorporated Fe^{II} high spin (HS) ions. [3] Furthermore, the absence of coupling patterns can be attributed to broadening by increased relaxation rates near the strong polar fields of the Fe^{II}(HS) ions.

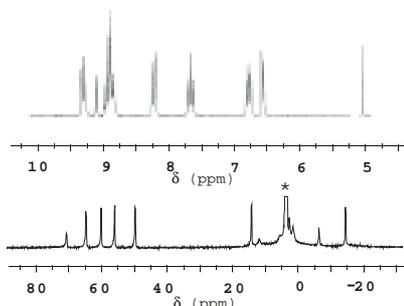


Figure 1: ¹H-NMR spectra of compounds **1** (top) and **3** (bottom) in [D₃]-acetonitrile (asterisk).

In solid state, the X-ray investigations of both complexes **2** and **3**, show pseudooctahedral N₆-surroundings for all Fe^{II}-ions (Figure 2). The averaged Fe-N bond lengths can be used as an indicator for the spin state, since the population of the anti-bonding e_g* orbitals in the HS case causes an elongation of the bond length by ca. 0.2 Å. [3] Thus, complex **2** shows at 120 K four identical Fe^{II}-N bond distances of d(Fe^{II}-N) = 1.95 Å, close to those characteristic of the Fe^{II}(LS) state.[4] Complex **3** exhibits at low temperature also three Fe^{II}-ions with LS characteristics, while the fourth one remains at bond lengths typically observed for the Fe^{II}(HS) state. Following the same argumentation, we can conclude that complex **3** presents at 293 K a situation pointing to three HS and one LS Fe^{II} sites.

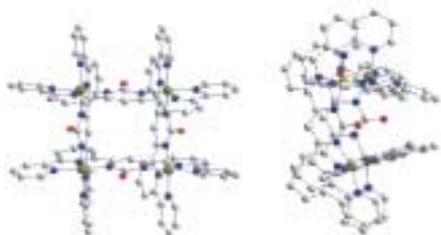


Figure 2: Top(left) and side (right) view of the single crystal X-ray investigation of complex **2** (anions, solvent molecules, and hydrogen atoms are omitted for clarity).

The solid state magnetic properties of the complexes **1-3** were examined directly by magnetic susceptibility

measurements. The diamagnetic compounds **1** and **2** did not show any magnetic moment. The magnetic properties of **3** are represented in Figure 3 in form of the $\chi_M T/4$ versus T curve, χ_M being the molar magnetic susceptibility, corrected for diamagnetic contributions ($\chi_D = -357.8 \cdot 10^6 \text{ cm}^3 \text{ mol}^{-1}$) using Pascal's constants, and T the temperature.

At room temperature, $\chi_M T/4$ is equal to $2.9 \text{ cm}^3 \text{ K mol}^{-1}$ and thus in the range of values expected for four HS Fe^{II} ions, since the spin-only value for a Fe^{II} ion in the HS state ($S = 2$) is $3.0 \text{ cm}^3 \text{ K mol}^{-1}$. On lowering the temperature, $\chi_M T/4$ progressively decreases reaching a value of $1.4 \text{ cm}^3 \text{ K mol}^{-1}$ at 30 K; below this temperature, $\chi_M T/4$ drops down. This can be attributed to zero-field splitting. [4] No hysteresis was detected, which is in line with the very gradual spin transition apparently arising from very weak cooperative interactions. [5]

We also investigated the magnetic properties of **3** under pressure. Pressure dramatically affects the SC curve, decreasing the $\chi_M T/4$ values over the whole temperature range (e.g. by $0.5 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K and 8.4 kbar). This corresponds to a shift of the SC curve to higher temperatures as a result of the lower volume for the LS Fe^{II} ions.

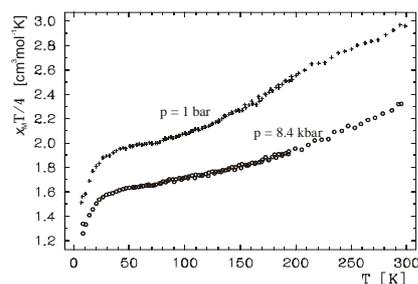


Figure 3: Magnetic susceptibility versus temperature plot of complex **3** at two different pressures.

The occurrence of spin transition in [2x2] grid-like complexes of the type $[\text{Fe}^{\text{II}}_4 \text{L}_4](\text{BF}_4)_n$ depends directly on the nature of the substituent R¹ in the 2-position of the ligand L. Compounds **1** and **2** with substituents in this position favoring strong ligand fields (R¹ = H; O) remain completely in the LS state at all temperatures studied. Only the complex **3** bearing a substituent which attenuates the ligand field sufficiently by steric effects (R¹ = Ph), exhibits, although incomplete, temperature triggered spin transition.

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