Spin Crossover

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# $Fe^{II}$ Spin-Crossover Phenomenon in the Pentadecanuclear $\{Fe_9[Re(CN)_8]_6\}$ Spherical Cluster**

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***Abstract:*** *The self-assembly of iron(II) ions with rare octacyanidorhenate(V) metalloligands in a methanolic solution results in the formation of a nanometric pentadecanuclear $\{Fe^{II}_9[Re^{V}(CN)_8]_6(MeOH)_{24}\}\cdot 10\,MeOH$ (**1**) molecule with a six-capped body-centered cubic topology. The cluster demonstrates a thermally-induced spin-crossover phase transition at $T_{1/2} = 195$ K which occurs selectively for a single $Fe^{II}$ ion embedded in the center of a cluster core.*

Molecule-based magnets, built of magnetically active metal complexes or organic radicals, have been intensively studied because of various magnetic properties, including magnetic ordering below the critical temperature ($T_c$),[1–3] spin-transition phenomena,[4–6] and slow magnetic relaxation.[7–9] Significant interest has been focused on cyanido-bridged bimetallic assemblies which exhibit magnetic coupling of a predictable strength, giving magnetic ordering at various $T_c$ values, in some cases up to 100 °C.[10–12] These systems were found to efficiently combine magnetism with other functionalities, such as ferroelectricity,[13] chirality,[14–17] luminescence,[18] sensitivity to guest molecules,[19–21] zero thermal expansion,[22] or photoinduced phase transitions.[24–26] The interaction between this additional property and magnetism gives rise to extra cross-effects.[27–30] We have shown magnetic second harmonic generation (MSHG),[31,32] light-induced spin-crossover magnetism,[23] and a 90° switching of the SHG polarization plane when chirality was coupled with photomagnetism.[14]

Magnetic materials based on polynuclear clusters have attracted particular attention as they can show a high-spin ground state leading to single-molecule magnetism (SMM)[33] or to a magnetocaloric effect.[34] Among such materials, bimetallic $[M(CN)_8]$-based clusters have great potential,[35] as demonstrated by a family of $\{M_9M'_6\}$ pentadecanuclear clusters $\{M^{II}_9[M'^{V}(CN)_8]_6(MeOH)_{24}\}$ (M = 3d metal; M′ = Mo, W; MeOH = methanol) which show a diverse range of magnetic functionalities, including high spin,[36–38] SMM,[39,40] and thermally induced charge transfer.[41,42]

In this regard, the application of the spin-crossover (SCO) effect to polynuclear molecules is rare. SCO was broadly investigated for mononuclear complexes, based mainly on the $Fe^{II}$ ion,[43,44] and coordination polymers offering efficient intramolecular interactions giving thermal hysteresis loops, crucial for applications such as memory devices.[45,46] Apart from a number of di- and tetranuclear species which demonstrate a spectacular multistep SCO effect,[47–50] there are only three well-characterized examples of larger SCO clusters: a) pentanuclear $\{[Fe^{II}(tmphen)_2]_3[M^{III}(CN)_6]_2\}$ (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline; M = Fe, Co),[51] b) heptanuclear $\{[Fe^{III}(salpet)]_6[Fe^{II}(CN)_6]\}Cl_2$ (salpet = a pendadentate Schiff base),[52] and c) tetradecanuclear $\{Fe^{II}_6[Cu^{I}(Tp^{4-py})]_8\}^{4+}$ ($Tp^{4\text{-}py}$ = tris{3-(4-pyridyl)-pyrazol-1-yl}hydroborate).[53] Other SCO clusters of $Fe^{III}$ ions with cyanidometallates, built of five to twelve centers, were characterized only by $^{57}Fe$ Mössbauer spectroscopy.[54,55] Thus, we focused our effort on the preparation of large SCO clusters which can be promising for both multistep SCO and cluster-based coordination polymers. Continuing our interest in $CN^-$-bridged $\{M_9M'_6\}$ clusters, we aimed to introduce SCO $Fe^{II}$ ions into this structure. Our previous attempt with $[W^{V}(CN)_8]^{3-}$ resulted in the formation of $\{Fe_9W_6\}$ molecule showing an iron(II)–tungsten(V) to iron(III)–tungsten(IV) charge-transfer (CT) process instead of an SCO effect.[41] We next used a rare $[Re^{V}(CN)_8]^{3-}$ molecule which was reported by J. R. Long et al.[56,57] as a product of thermal decomposition

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of $[Re^{IV}(CN)_7]^{4-}$ in the presence of $KIO_4$ and $MnCl_2$. Its voltammetry suggested that $[Re^{V}(CN)_8]^{3-}$ has an accessible $Re^{VI}$ instead of a $Re^{IV}$ oxidation state.[56] Thus, it should stabilize the $Fe^{II}$ state, providing an opportunity to potentially detect the SCO effect on a 3d metal center. Following this procedure, we report the structure and properties of a $\{Fe^{II}_9[Re^{V}(CN)_8]_6(MeOH)_{24}\}\cdot 10\,MeOH$ (**1**) cluster showing an $Fe^{II}$ spin-crossover effect, demonstrated by temperature-dependent structural, spectroscopic, and magnetic studies.

Yellow crystals of **1** were obtained by the self-assembly of $Fe^{II}$ chloride with an organic salt of $[Re^{V}(CN)_8]^{3-}$ in methanol (see Figure S1 in the Supporting Information and details therein). Single-crystal X-ray diffraction was performed at 240(2) and 120(2) K.[60] The related high- and low-temperature phases are denoted $\mathbf{1}^{HT}$ and $\mathbf{1}^{LT}$, respectively. $\{Fe^{II}_9[Re^{V}(CN)_8]_6(MeOH)_{24}\}$ (**1**) consists of $CN^-$-bridged $\{Fe_9Re_6\}$ clusters of a six-capped body-centered cubic topology, analogous to other members of the $\{M^{II}_9[M'^{V}(CN)_8]_6(MeOH)_{24}\}$ family (M = 3d metal, M′ = Mo, W; see Figure 1 and Table 1 and Figures S2–S3 and Tables S1–S3 in the Supporting Information).[36–42] This molecule comprises one $[Fe^{II}(NC)_6]^{4-}$ complex (containing atom Fe1) located in the center of a cube, where corners are occupied by eight $[Fe^{II}(MeOH)_3(NC)_3]^-$ ions, involving four crystallographically unique Fe sites (Fe2–Fe5). Six $[Re^{V}(CN)_8]^{3-}$ units cap the faces of the Fe-based cube which completes the almost spherical cluster (Figure 1).

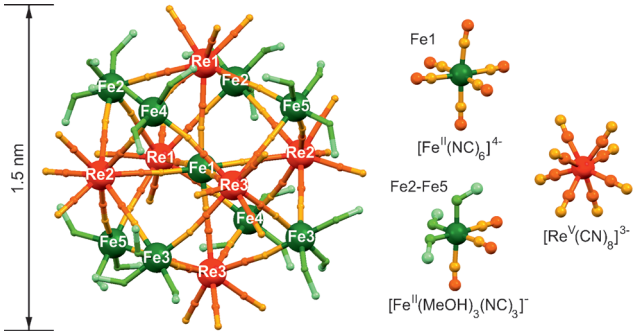


***Figure 1.*** The structure of the cluster $\{Fe^{II}_9[Re^{V}(CN)_8]_6(MeOH)_{24}\}$ (**1**) and detailed views of the coordination geometry of the $Fe^{II}$ and $Re^{V}$ complexes embedded in the cluster core.

The average Fe–N/O bond lengths at high ($\mathbf{1}^{HT}$) and low temperature ($\mathbf{1}^{LT}$) are given in Table 1. In $\mathbf{1}^{HT}$, the average Fe–N distance for Fe1 is close to 2.06 Å, whereas for the Fe2–Fe5 centers the mean lengths of Fe–N/O bonds are in the range 2.13–2.14 Å. These lengths are in good agreement with values measured in octahedral high-spin $Fe^{II}$ centers ($^{HS}Fe^{II}$) in $CN^-$-bridged systems.[14,41] In $\mathbf{1}^{LT}$, the Fe–N/O distances for Fe2–Fe5 atoms decrease gradually because of a standard thermal contraction. On the contrary, the Fe1–N bond lengths change by approximately 6% to give a mean value of 1.93 Å which can be assigned to a low-spin $Fe^{II}$ center ($^{LS}Fe^{II}$).[4,14] This suggests that **1** demonstrates the spin-crossover effect selectively for internal Fe1 centers whereas the external Fe2–Fe5 sites remain in the high-spin state because of differences in their coordination spheres. Fe1 coordinates six $CN^-$ ligands through the N atoms, which gives an intermediate ligand-field strength suitable in magnitude for the SCO effect to occur, as shown for Prussian Blue analogues.[58] Fe2–Fe5 sites have a mixed $N_3O_3$ coordination geometry, resulting in insufficient ligand-field strength for the SCO effect to occur.[58]

***Table 1:*** Average Fe–N/O bond lengths [Å] for **1**.

| T/K | Fe1 | Fe2 | Fe3 | Fe4 | Fe5 |
|---|---|---|---|---|---|
| 240(2), $\mathbf{1}^{HT}$ | 2.06(1) | 2.13(1) | 2.14(1) | 2.14(1) | 2.13(1) |
| 120(2), $\mathbf{1}^{LT}$ | 1.93(1) | 2.12(1) | 2.13(2) | 2.13(2) | 2.12(1) |

The structural transition on Fe1 sites implies changes in other metric parameters of the cluster (Table S2). On cooling from $\mathbf{1}^{HT}$ to $\mathbf{1}^{LT}$, the mean Fe1–Re distance is decreased by circa 1.5%, whereas smaller decreases of 0.4% are found for other Fe–Re bridges. All Re–C bond lengths remain unchanged, and the dodecahedral geometry of $[Re^{V}(CN)_8]^{3-}$ is preserved (Table S3). It suggests that the $Re^{V}$ state is stable during the transition, and the cyanide complex serves only as a flexible mediator in the propagation of the SCO effect. The structural transition in a cluster is accompanied by the shortening of intercluster $Fe{-}O_{MeOH}\cdots NC{-}W$ hydrogen bonds, and the expected unit-cell compression from 16236.2(7) to 15675.7(15) $Å^3$ ($\approx$3.5%) is detected (Figure S3).

On cooling from $\mathbf{1}^{HT}$ to $\mathbf{1}^{LT}$, the color of the crystals changed from yellow to blue. This is connected with the appearance of a low-spin $Fe^{II}$ center which gives rise to strong absorption of visible light as a result of their d–d transitions (Figure S1). The analysis of the Fe oxidation state in $\mathbf{1}^{HT}$ and $\mathbf{1}^{LT}$ was performed by $^{57}Fe$ Mössbauer spectroscopy (Figure 2). The spectrum at 295 K was deconvoluted into two doublets ascribed to high-spin $Fe^{II}$ with isomer shifts of $\delta = 1.25(1)$ and 1.39(1) $mm\,s^{-1}$ (Table 2).[4] The broad line component is assigned to Fe2–Fe5 sites of four slightly different quadrupole splitting values. The inner doublet indicates the crystallographically different Fe1 site. This component transforms at 80 K into the doublet at $\delta = 0.46\ mm\,s^{-1}$ with a very small quadrupole splitting of $\Delta E_Q = 0.12\ mm\,s^{-1}$ which is attributable to the low-spin $Fe^{II}$ center. The relative intensity of the signal attributable to the low-spin $Fe^{II}$ is $8 \pm 2$% which agrees well with the structural studies showing that only one Fe center in the $\{Fe_9Re_6\}$ cluster exhibits the SCO effect. The remaining doublets attributable to the high-spin $Fe^{II}$ center show the characteristic behavior for a $3d^6$ configuration, that is an increase in quadrupole splitting with decreasing temperature. Moreover, the Fe2–Fe5 states are divided into two groups characterized by two doublets with an intensity ratio of 1:3. This indicates that the ligand arrangement around one of these states, probably Fe2, is different, as suggested by structural studies (Table S3).

The SCO transition in **1** influences the magnetic properties of the cluster (see Figure 3 and Figures S4 and S5). The room-temperature product of magnetic susceptibility and temperature ($\chi_M T$) is 33.7 $cm^3\,mol^{-1}\,K$ for the $\{Fe_9Re_6\}$ unit which corresponds to nine uncoupled high-spin $Fe^{II}$ centers ($S = 2$) separated by a diamagnetic $[Re^{V}(CN)_8]^{3-}$ unit.[56] The

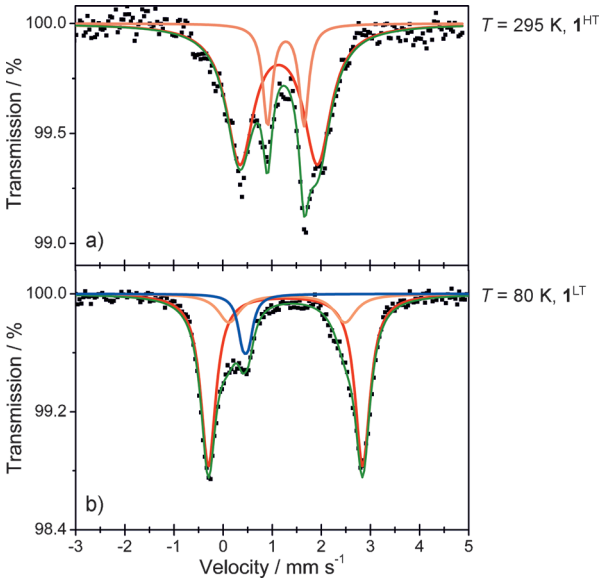


***Figure 2.*** $^{57}$Fe Mössbauer spectra of **1** at a) 295 K and at b) 80 K. Experimental results are shown as black data points. The fitted results are shown as solid lines. Colors: $^{LS}Fe^{II}$ (blue), $^{HS}Fe^{II}$ (red and orange), total calculated fit (green).

***Table 2:*** $^{57}$Fe Mössbauer spectral parameters for **1**.

| $T$ [K] | Fe site | $\delta$ [mm s$^{-1}$] | $\Delta E_Q$ [mm s$^{-1}$] | Area contribution [%] |
|---|---|---|---|---|
| 295(1), **1**$^{HT}$ | HS Fe$^{II}$ | 1.25(1) | 1.58(2) | 80(4) |
| | HS Fe$^{II}$ | 1.39(1) | 0.74(2) | 20(4) |
| 80(1), **1**$^{LT}$ | HS Fe$^{II}$ | 1.30(1) | 3.14(2) | 70(2) |
| | HS Fe$^{II}$ | 1.27(1) | 2.36(2) | 22(2) |
| | LS Fe$^{II}$ | 0.46(1) | 0.12(2) | 8(2) |

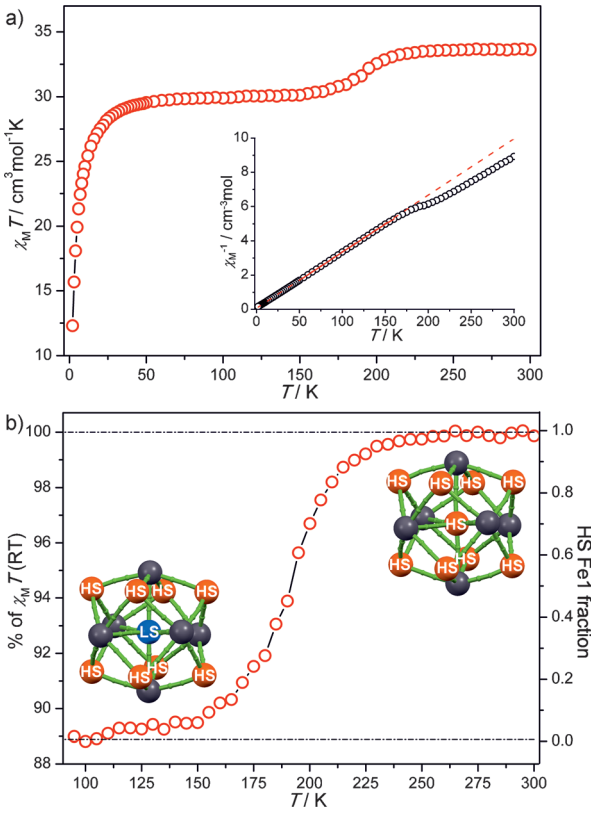


***Figure 3.*** a) Plot of $\chi_M T$ values versus temperature ($T$) with the Curie–Weiss law fit (red line) for **1** ($H_{dc}$ = 1000 Oe). Inset in (a): $\chi_M^{-1}$ values plotted against $T$. b) The related $T$ dependence of the relative decrease in the $\chi_M T$ value compared with the room-temperature value (% of $\chi_M T$(RT)) which corresponds to the Fe1 HS fraction.

average $g$ value of Fe$^{II}$ is 2.23 which is in the 2.2–2.3 range, typical for CN$^-$-bridged systems with high-spin Fe$^{II}$ centers.[14,41] On cooling, the $\chi_M T$ value remains unchanged to 220 K, later decreases strongly over the next 60 K, reaching 30.2 cm$^3$ mol$^{-1}$ K at 160 K. On further cooling, the decrease is slow to 30 K, and much faster below this point (Figure 3). The first decrease of the $\chi_M T$ value can be assigned to the spin crossover resulting in the transition from high-spin Fe$^{II}$ ($S = 2$) to low-spin Fe$^{II}$ ($S = 0$). The signal at 160 K is 89.6 % of the room-temperature value, which is in good agreement with the approximate 11 % decrease expected for the SCO occurring on a single Fe of the cluster (specifically Fe1). Thus, the relative decrease of the $\chi_M T$ value in comparison to the room-temperature value shows the temperature dependence of the Fe1 high-spin fraction. On increasing the temperature, the plot corresponds to the cooling data, with no thermal hysteresis observed. Considering the decrease in $\chi_M T$ value in the 220–160 K range, the largest change occurs within 20 K (205–185 K), and the transition temperature, measured from the temperature dependence of the first derivative of $\chi_M T$, is $T_{1/2} = 195$ K (Figure S4). The magnetization at $T = 1.8$ K as a function of magnetic field is not saturated at 50 kOe and reaches 25.6 Nβ, which is lower than the 35.7 Nβ expected for eight isolated high-spin Fe$^{II}$ centers (Figure S5). This result, together with the abrupt decrease of the $\chi_M T$ value below 20 K and a negative value of the Weiss constant $\theta = -1.8$ K (obtained from the Curie–Weiss law fit to data in the 50–160 K range), confirm the occurrence of antiferromagnetic interactions which presumably lead to a zero-spin cluster at very low temperatures.

In conclusion, we have prepared a fifteen-metal-centered cyanido-bridged {Fe$^{II}_9$[Re$^{V}$(CN)$_8$]$_6$(MeOH)$_{24}$} (**1**) nanoball which is the highest nuclearity molecule reported exhibiting the spin-crossover effect.[4] **1** exhibits a $^{HS}Fe^{II} \leftrightarrow {}^{LS}Fe^{II}$ spin transition at $T_{1/2} = 195$ K which is induced selectively on a single Fe$^{II}$ center embedded in a {Fe(NC)$_6$} unit in the center of a cluster. In contrast, the remaining eight Fe$^{II}$ sites of the {Fe$_9$Re$_6$} cluster remain in the high-spin state because of mixed {FeN$_3$O$_3$} coordination. This selective spin-crossover effect was achieved by rational design based on our previous results with the analogous {Fe$_9$W$_6$} and {Fe$_6$Co$_3$W$_6$} clusters.[41,42] Our molecule potentially opens the way for a new class of SCO polynuclear systems. The challenge now is to induce the SCO effect on external Fe sites of a cluster core, which may be achieved by the coordination of appropriate N-donor ligands to replace labile, coordinated solvent molecules, as was reported for other members of the family of {M$_9$M′$_6$} clusters.[35,59] Alternatively, it should be possible to control the spin state of Fe sites using pressure or light irradiation.[14] Further studies along this line are in progress.

  

**Keywords:** cluster compounds · cyanide ligands · iron · rhenium · spin crossover

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