Cooperative Spin Crossover Behavior in Cyanide-Bridged Fe(II)−M(II) Bimetallic 3D Hofmann-like Networks (M = Ni, Pd, and Pt)

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Phase transitions have always interested the scientific community from a fundamental point of view, but they have also been of interest because of their possible applications.[2] In the field of molecular magnetism,[3] spin crossover complexes are a singular kind of switchable materials.[4,5] Among them, iron(II) spin crossover complexes have attracted much attention.[6] They change from a diamagnetic ($S = 0$) low-spin state (LS) to a paramagnetic ($S = 2$) high-spin state (HS) in response to a temperature or pressure gradient and by light irradiation. Their optical properties are also very different in each spin state, and, in particular, when no charge transfer transition occurs in the visible region, they change color dramatically upon spin conversion.

The cooperative nature of the spin conversion has stimulated much research because first-order transitions and thermal hysteresis confer to these systems a potential memory effect.[7] Cooperativity stems from the different molecular size and shape associated with the two spin states. This structural change is concomitant with the electronic transfer of two electrons between the e_g and t_{2g} orbitals which accompanies the spin conversion. Thus, cooperativity can be considered as a measure of the efficacy of transmitting these changes, via intermolecular interactions, in the whole molecular crystal. However, the synthesis of one- (1D), two- (2D), and three-dimensional (3D) coordination polymers has become an alternative way to explore and/or magnify cooperativity as intermolecular forces are difficult to control.[4,5,8,9] Only one three-dimensional (3D) spin crossover compound of formula $[\mathrm{Fe(btr)_3(ClO_4)_2}]$ (btr = 4,4′-bis-1,2,4-triazole) has been reported.[10]

The 2D coordination polymer compound $[\mathrm{Fe(py)_2Ni(CN)_4}]$ (**1a**) (py = pyridine) was reported five years ago.[11] In this system the $[\mathrm{Ni(CN)_4}]^{2-}$ moiety acts as an anionic ligand complex in the same fashion as $\mathrm{NCS^-}$ or $\mathrm{NCSe^-}$ do in many iron(II) spin crossover compounds, the main difference being its ability to allow polymerization in two dimensions. **1a** is a modification of a relevant class of compounds known as Hofmann clathrate compounds.[12] **1a** consists of 2D extended metal cyanide sheets constructed by the alternate linkage between square-planar Ni(II) and octahedral Fe(II) ions through cyano bridges. The Fe(II) ion is octahedrally coordinated by four terminal N atoms of the cyano groups and two N atoms of two py ligands in a trans configuration.[11] **1a** undergoes a cooperative spin transition between 210 and 170 K.

Taking into account the magnetic behavior of **1a** we have decided to use suitable bis-monodentate pyridine-like ligands in order to achieve 3D dimensionality in new spin crossover compounds and explore the influence of dimensionality on cooperativity. In the present communication we report the syntheses and preliminary characterization of the novel coordination spin crossover polymers of formula $[\mathrm{Fe(pz)M(CN)_4}]\cdot n\mathrm{H_2O}$ [pz = pyrazine; M = Ni(II), ($n = 2$) (**2a**); Pd(II) ($n = 2.5$), (**2b**); and Pt(II) ($n = 2$), (**2c**)]. They precipitate when a solution of $\mathrm{K_2[M'(CN)_4]}$ in $\mathrm{H_2O}$ is added with constant stirring to a solution which contains stoichiometric amounts of pz and $\mathrm{Fe(BF_4)_2\cdot 6H_2O}$ in MeOH/$\mathrm{H_2O}$ (1:1). Due to insolubility **2a** appears as a poorly crystalline solid whereas **2b** and **2c** are crystalline powders, which have exactly the same X-ray powder diffraction pattern. Ab initio crystal structure studies were carried out in order to confirm their 3D nature in the absence of single crystals.[13] As expected, the structure of the pz derivatives differs from that of **1a** in that the pz ligands bridge the iron atoms of consecutive sheets achieving a pillaring of the 2D sheets by vertical columns of the pyrazine bridge to give a 3D structure (see Figure 1). Similar structural motives have been already observed by Iwamoto et al. when aliphatic didentate amines were used in the Cd−$[\mathrm{Ni(CN)_4}]^{2-}$ system.[14] For comparison, we have also synthesized and characterized the corresponding Pd (**1b**) and Pt (**1c**) derivatives of **1a**. The synthesis of **1b** and **1c** was as for **2a**−**c** but using an excess of py instead of pz. **1b** and **1c** precipitated as poorly crystalline solids. The analytical data agree well with the formula $[\mathrm{Fe(py)_2(M(CN)_4)}]$ (M = Pd and Pt). This fact, together with the magnetic and calorimetric studies, allows us to consider them isostructural to **1a**.

The magnetic susceptibility, χ_M, for **2a**−**c** was determined over the 5−350 K range in a field of 1 T. The $\chi_M T$ versus T plot (where T is the temperature) is shown in Figure 2. In the high-temperature region the $\chi_M T$ values are in the range 3.2−3.8 cm^3 K mol^{-1} for **1** and **2**. These values are consistent with a $S = 2$ HS ground state for iron(II). Upon cooling, $\chi_M T$ remains almost constant down to a temperature value from which it undergoes a sharp decrease characteristic of a first-order spin transition. For **2b** and **2c** the conversion to the LS state is virtually complete. However, for **2a**, **1b**, and **1c** around 15% molecules remain trapped in the HS state at low temperatures. The warming mode reveals the occurrence of thermal hysteresis. The critical temperatures for

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[13] Crystal structure analysis: $\mathrm{C_8H_4N_6O_2FePt}$, $M = 467.097$ g mol^{-1}, tetragonal, space group $P4/m$, $a = b = 7.4144(5)$ Å, $c = 7.2141(6)$ Å, $V = 396.58$ Å^3, ρcalc = 1.955 g cm^{-3} for $Z = 1$.

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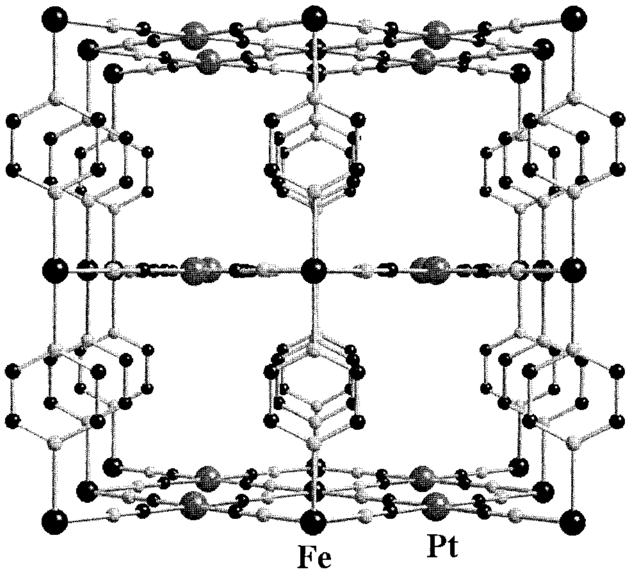

Figure 1. Perspective view of the structure of $[Fe(pz)Pt(CN)_4]\cdot 2H_2O$ (**2c**). Fe−N(pz) = 2.267(4) Å; Fe−NC = 2.114(5) Å; Pt−CN = 1.972(5) Å; C−N = 1.158(6) Å; C−N(pz) = 1.392(2) Å; C−C(pz) = 1.419(5) Å; Fe−Fe = 7.2141(6) Å; Fe−Pt = 5.2432(6) Å.

the cooling (T_c^{down}) and warming (T_c^{up}) modes are 186 and 195 K (**1a**),[11] 280 and 305 K (**2a**), 233 and 266 K (**2b**), 220 and 240 K (**2c**), 208 and 213 K (**1b**), and 208 and 216 K (**1c**), respectively. The significantly higher T_c values observed for **2a**−**c** with respect their py counterparts **1a**−**c** cannot be explained in terms of "simple" ligand field theory as py imparts a stronger ligand field than pz. Thus, the internal pressure originated from the more rigid 3D structures can be responsible for the effective stronger ligand field at iron(II) sites observed for **2a**−**c**. Similarly, a difference in dimensionality can be the reason for the significantly wider hysteresis loops observed for **2a**−**c** with respect to **1a**−**c** 2D systems. Interestingly, these compounds undergo a dramatic change of color from white, pale-yellow, or orange in the HS state to garnet in the LS state. This thermochromic effect previously reported for other spin crossover compounds arises from the different electronic absorption spectra of the LS and HS species.[4,6]

Differential scanning calorimetry (DSC) measurements were carried out in order to evaluate the enthalpy (ΔH) and entropy (ΔS) variations associated with the spin transitions of **2a**−**c**, **1b**, and **1c**. The dependence of the molar heat capacity, C_p, shows a typical anomaly at $T_c^{down} = 279$ K and $T_c^{up} = 295$ K for **2a**. A C_p vs T plot shows two maximums in the cooling and warming modes for **2b** [$T_{c1}^{down} = 256$ K, $T_{c2}^{down} = 238$ K, $T_{c1}^{up} = 265$ K, $T_{c2}^{up} = 290$ K] and three maximums in the cooling mode [$T_{c1}^{down} = 258$ K, $T_{c2}^{down} = 226$ K, $T_{c3}^{down} = 216$ K] and two in the warming mode [$T_{c1}^{up} = 252$ K, $T_{c2}^{up} = 289$ K] for **2c**. The estimated average ΔH and ΔS parameters are 14.5 kJ mol^{-1} and 51 J K^{-1} mol^{-1} (**2a**), 21 kJ mol^{-1} and 83 J K^{-1} mol^{-1} (**2b**), and 21 kJ mol^{-1} and 81 J K^{-1} mol^{-1} (**2c**), respectively. The singularities observed in the C_p vs T curves, which are also reflected in the $\chi_m T$ versus T plots, together with their considerably great ΔH and ΔS average values estimated indicate the occurrence of a crystallographic phase transition in addition to a spin state transition for **2b** and **2c**.[15] **1b** and **1c** display very similar DSC curves with one singularity. The average ΔH and ΔS values, extrapolated at 100% of spin conversion, are 14.6 kJ mol^{-1} and 69 J K^{-1} mol^{-1}.

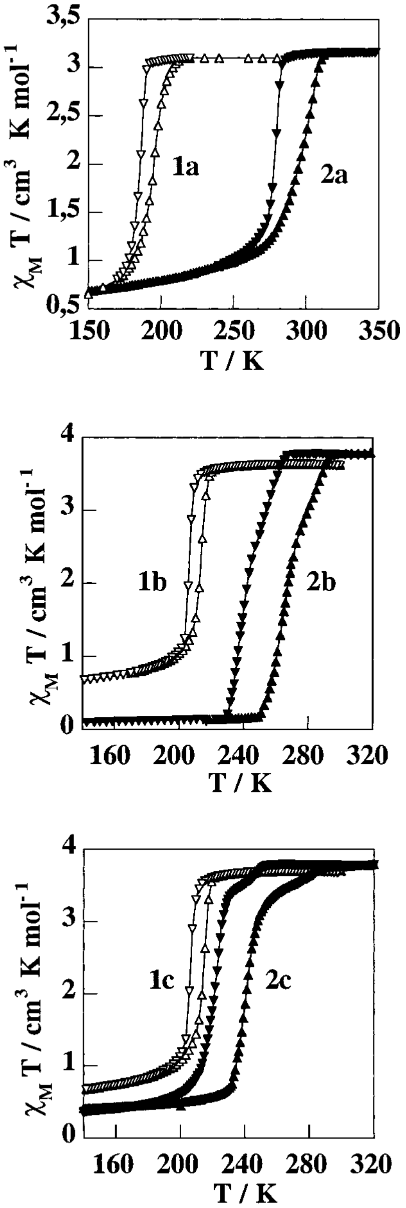

Figure 2. $\chi_M T$ vs T plot for **1** and **2**. The magnetic data of **1a** has been taken from ref 11.

This communication illustrates, for the first time, how the change of dimensionality from 2D to 3D in two tightly related systems influences cooperativity. Additionally, the coordination spin crossover 3D polymers here reported belong to an important class of porous systems able to accept guest molecules in the cavities. Hence, they represent a good opportunity to study systematically the role of different guest molecules on the nature of the spin transition.

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Supporting Information Available: Listings of X-ray crystallographic data in CIF format. Analytical, IR, and calorimetric data. This material is available free of charge via the Internet at http://pubs.acs.org.

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