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{$Fe(3CNpy)_2[Cu(3CNpy)(\mu\text{-}CN)_2]_2$}: a One-Dimensional Cyanide-Based Spin-Crossover Coordination Polymer

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A novel one-dimensional coordination polymer made up of Fe^{II}, 3-cyanopyridine (3CNpy), and the singular in situ formed $[Cu^{I}(3CNpy)(CN)_2]^-$ anionic bridge has been synthesized. This compound undergoes a spin-crossover behavior according to its magnetic and calorimetric properties. The crystal structure of the title compound has been studied in the high- and low-spin states and correlated with the character of the spin conversion. Evidence for intense spin-state-dependent Cu····Cu interactions between the chains is also reported.

Cyanide-bridged homo- and heterometallic coordination polymers have been shown to exhibit a remarkable diversity of structural types with interesting magnetic, electrochemical, magnetooptical, thermomechanical, and zeolitic properties.[1] In particular, Hofmann-like clathrate compounds[2] containing Fe^{II} ions have led to the development of a number of two-dimensional (2D) {$Fe(pyridine)_2[M^{II}(CN)_4]$}[3,4a] and three-dimensional (3D) {$Fe(pyrazine)[M^{II}(CN)_4]$}$\cdot nH_2O$[4a] frameworks with M^{II} = Ni, Pd, and Pt. The pyrazine derivatives undergo abrupt thermal-, pressure-, and light-induced spin-crossover[5] (SCO) behavior with thermal hysteresis close to room temperature,[4a−c] which confers them bistability, an essential property for the construction of advanced materials with potential applications. The formal replacement of the $[M^{II}(CN)_4]^{2-}$ anions by $[M^{I}(CN)_2]^-$ groups (M^I = Cu, Ag, Au), with *trans*-bispyridylethylene, 4,4′-bipyridine, 3-cyanopyridine (3CNpy), or pyrimidine (pmd) as ligands, has afforded new 2D and 3D SCO polymers.[6] Such compounds not only display interesting pressure- and light-induced properties[6e,f] but also can combine their cooperative spin transition properties (magnetic, chromatic, and structural) with different chemical properties such as crystalline-state ligand-substitution reactions with allosteric effects,[4c] metallophilicity,[6d] or host−guest interactions.[7]

Most of the above referred $Fe^{II}L[M^{I}(CN)_2]$ systems are based on the $[Ag(CN)_2]^-$ or $[Au(CN)_2]^-$ building blocks. In fact, only one SCO coordination polymer based on $[Cu(CN)_2]^-$ has been investigated so far.[6b] Herein we report the synthesis,[8] crystal structure, and magnetic and calorimetric properties of {$Fe(3CNpy)_2[Cu(3CNpy)(\mu\text{-}CN)_2]_2$} (**1**), which rep-

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(8) Synthesis of **1** was performed under an argon atmosphere using a slow-diffusion technique. One side of an H-shaped vessel contains a mixture of $FeCl_2\cdot 4H_2O$ (0.25 mmol, 50 mg) and 3CNpy (1 mmol, 107 mg) in methanol−water (1:1; 2 mL). The other side contains a water solution (2 mL) of $KCu(CN)_2$ (0.5 mmol, 77.8 mg). Prismatic orange crystals were obtained after 3 weeks. Yield: 55%. Anal. Calcd for $C_{28}H_{16}N_{12}FeCu_2$: C, 47.76; H, 2.27; N, 23.88. Found: C, 47.53; H, 2.21; N, 24.01.

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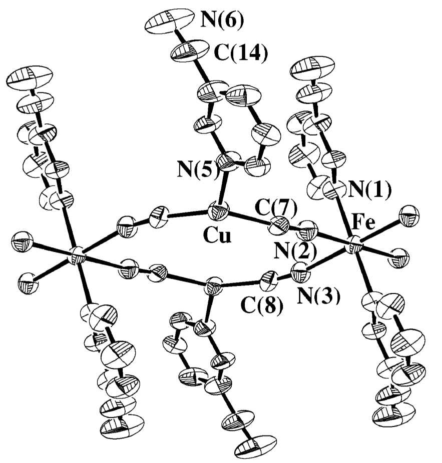

Figure 1. Molecular fragment of **1** including the relevant non-hydrogen atom numbering. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms were omitted for clarity.

resents the first example of a cyanide-based one-dimensional (1D) SCO polymer.

The crystal structure of **1** has been investigated at 293 and 130 K.[9] Compound **1** crystallizes in the triclinic $P\bar{1}$ space group and at whatever temperature it does not change symmetry. The structure made up of a self-assembly of Fe^{II}, 3CNpy, and $[Cu(CN)_2]^-$ units forms infinite chains. There are two different coordination centers in the chain (Figure 1). One stems from the coordination of the Cu atom of the $[Cu(CN)_2]^-$ group by the 3CNpy ligand to give $[Cu(3CNpy)(CN)_2]^-$ building blocks in which the Cu^I ion is essentially three-coordinate. Consequently, the $[Cu(CN)_2]^-$ moiety strongly deviates from linearity because the coordination geometry of Cu^I is actually trigonally distorted. The bond distances and angles are respectively Cu−C(7) = 1.933(6) Å, Cu−C(8) = 1.960(6) Å, and Cu−N(5) = 2.081(6) Å and N(5)−Cu−C(7) = 121.2(2)°, N(5)−Cu−C(8) = 111.7(2)°, and C(7)−Cu−C(8) = 119.1(3)° at 293 K. The Cu^I atom is 0.329(1) Å out of the average plane defined by the atoms C(7), C(8), and N(5). The Fe^{II} atom located at an inversion center defines a pseudooctahedral $[FeN_6]$ coordination core whose equatorial positions are occupied by the cyanide N atom belonging to the $[Cu(3CNpy)(CN)_2]^-$ bridging group, while the remaining apical positions are occupied by the pyridine N atom of two additional 3CNpy groups. The axial Fe−N bonds [Fe−N(1) = 2.239(5) and 2.014(4) Å for 293 and 130 K, respectively] are longer than those of the equatorial positions [Fe−N(2) = 2.129(5) and 1.963(4) Å and Fe−N(3) = 2.162(5) and 1.963(4) Å for 293 and 130 K, respectively]. The average $[FeN_6]$ bond length variation is 0.196 Å, a value that is close to what is expected for the

(9) Crystal data for **1**: $C_{28}H_{16}N_{12}FeCu_2$, M_w = 703.46, triclinic, space group $P\bar{1}$ (No. 2). At 130(2) K (deep-red color), a = 6.8490(3) Å, b = 7.7800(4) Å, c = 13.7260(8) Å, α = 73.765(2)°, β = 84.770(2)°, γ = 80.681(2)°, V = 692.15(6) Å^3, Z = 1, D_{calc} = 1.686 g cm^{-3}, μ = 2.083 mm^{-1}, λ(Mo Kα) = 0.710 73 Å, 5444 reflections collected, 2231 independent reflections with $I > 2\sigma(I)$ [R_{int} = 0.0479], R1 = 0.0545, wR2 = 0.1151 [$I > 2\sigma(I)$]. At 293(2) K (orange color), a = 6.9260(3) Å, b = 8.0610(3) Å, c = 13.9690(6) Å, α = 73.533(2)°, β = 89.662(2)°, γ = 81.120(2)°, V = 738.35(5) Å^3, Z = 1, D_{calc} = 1.582 g cm^{-3}, μ = 1.953 mm^{-1}, λ(Mo Kα) = 0.710 73 Å, 5031 reflections collected, 1913 independent reflections with $I > 2\sigma(I)$ [R_{int} = 0.0467], R1 = 0.0586, wR2 = 0.1622 [$I > 2\sigma(I)$].

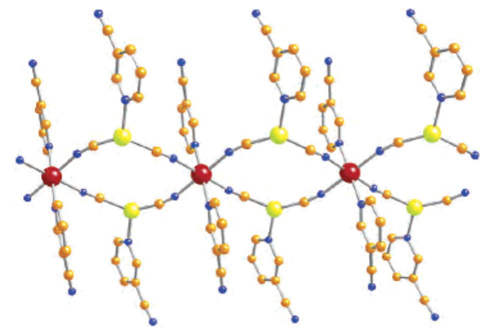

Figure 2. Perspective view of the 1D polymer **1**: red, Fe; yellow, Cu; blue, N; orange, C.

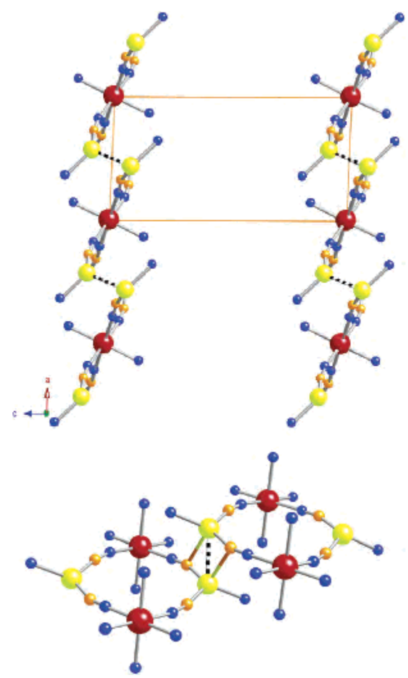

Figure 3. Schematic view of the chains seen along the *b* direction defining a 2D packing (top). Close contacts between two chains (bottom): (i) the short $Cu^I\cdots Cu^I$ contacts are represented as white and black bonds; (ii) the yellow-orange lines correspond to the short Cu···C(8)^{ii} contacts. The 3CNpy ring [except the N(1) and N(5) atoms] has been omitted for simplicity.

structural modification associated with a spin transition according to the magnetic and calorimetric behavior (see below). A given Fe^{II} atom is connected to two adjacent Fe^{II} centers through four crystallographically equivalent $[Cu(3CNpy)(CN)_2]^-$ bridges, giving the mentioned infinite chains running along the [010] direction (Figure 2). The chains are organized in such a way that they form parallel layers lying in the *ab* plane separated by c = 13.9690(6) Å [the distance Fe····Fe^i ($i = x, y, 1 + z$); Figure 3, top]. Within a layer, short interchain $Cu^I\cdots Cu^I$ contacts are observed. These contacts are significantly smaller than the corresponding van der Waals radii sum 2.8 Å and are temperature-dependent: 2.6358(15) and 2.5906(11) Å at 293 and 130 K, respectively. The proximity of the $[Cu(3CNpy)(CN)_2]^-$ groups allows additional weak interactions between the C(8) and Cu^I atoms of the adjacent chains (Figure 3, bottom). The Cu^I−C(8)^{ii} coordination distance, 2.416(6) Å at 293 K ($ii = 1 - x, 2 - y, -z$), significantly larger than those lying in the trigonal plane, is temperature-dependent and shortens

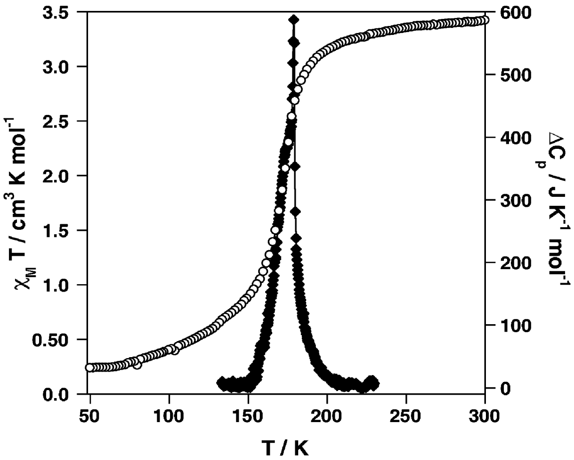

Figure 4. $\chi_M T$ vs T curve (white circles) and temperature dependence of ΔC_p (black diamonds) for **1**.

by 0.038(6) Å upon cooling from 293 to 130 K. Observation of short $M^I \cdots M^I$ contacts in group 11 is usually associated with the occurrence of metallophilic interactions.

This is particularly true for compounds involving Ag^I and Au^I atoms where relativistic effects are expected to be more important than in Cu^I compounds. The nature of intermolecular $Cu^I \cdots Cu^I$ interactions has been recently discussed from a theoretical and structural database analysis.[10] From this structural analysis, the authors conclude that the shortest intermolecular $Cu^I \cdots Cu^I$ contact observed is 2.71 Å, a value that is significantly larger than that observed in the title compound, 0.074 and 0.119 Å for the high- and low-spin states, respectively. However, from a theoretical viewpoint, it is difficult to conclude that short $Cu^I \cdots Cu^I$ distances correspond to attractive intermetallic interactions because they are expected to be very weak.

It is interesting to compare the structure of the title compound with that of the 2D SCO coordination polymer $\{Fe(pmd)_2[Cu(CN)_2]_2\}$.[6b] In both cases, the tendency to expand the coordination number of Cu^I from two to three is fulfilled differently. The pmd acts as a bridging ligand coordinating one Cu^I and one Fe^{II} of the adjacent $\{Fe[Cu(CN)_2]_2\}_\infty$ chains, originating a 2D coordination polymer with the topology of $CdCl_2$. In the present case, the 3CNpy group could formally act as a bridging ligand in a similar way as pmd does. However, the N atom of the nitrile group is much less a donor than that of pmd; consequently, 3CNpy only coordinates the Fe^{II} and Cu^I atoms through the pyridine N. Thus, during the crystallization process, the $[Cu(3CNpy)(CN)_2]^-$ anions were formed in solution to give the title 1D polymer **1**.

The thermal dependence of the product $\chi_M T$ (χ_M being the molar magnetic susceptibility and T the temperature) and the anomalous heat capacity, ΔC_p, for **1** are displayed in Figure 4. $\chi_M T$ is equal to 3.42 cm^3 K mol^{-1} at 300 K, which is in the range of the values expected for an Fe^{II} ion in the high-spin state. Upon cooling, $\chi_M T$ decreases slightly down to ca. 210 K, after which it undergoes a complete high-spin $\leftrightarrow$ low-spin spin transition. The characteristic T_c value is estimated to be 172 K. Cooling and warming modes reveal the lack of thermal hysteresis.

The calorimetric measurements were carried out in the 120−300 K temperature range. It displays a sharp peak at 179 K with a more rounded shoulder at ca. 174 K. These temperatures agree reasonably well with the T_c value observed from the $\chi_M T$ vs T plot. The enthalpy (ΔH) and entropy (ΔS) variation associated with the spin transition are $\Delta H = 7.9 \pm 0.4$ kJ mol^{-1} and $\Delta S = 45 \pm 3$ J K^{-1} mol^{-1}, which are within the normal limits observed for Fe^{II} SCO compounds.

It deserves to be noted that **1** does not undergo a strong cooperative spin transition, in contrast to $\{Fe(pmd)_2[Cu(CN)_2]_2\}$, which displays a hysteresis of ca. 10 K. This is most likely due to the 2D nature of the latter compound, which confers it a more rigid structure. Although the Cu···Cu interchain interactions could be considered an efficient source of cooperativity in **1**, the chains are flexible enough because the Fe−N−C−Cu angles change significantly during SCO in **1**, i.e., 8.8(5)° for Fe−N(2)−C(7) and 3.3(6)° for Cu−C(8)−N(3). Comparable changes have been observed in the Fe−N(CS) bending angles of the $[Fe(tap)_2(NCS)_2]\cdot nCH_3CN$ complex upon SCO.[11] These intrachain modifications probably absorb instead of transmitting the structural changes, associated with the $[FeN_6]$ sites, mitigating the cooperativeness of the spin transition. Similar effects have been reported previously for 1D polymers bearing tetrazole groups.[12]

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Supporting Information Available: Crystallographic information file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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