A Charge-Transfer-Induced Spin Transition in the Discrete Cyanide-Bridged Complex {[Co(tmphen)₂]₃[Fe(CN)₆]₂}

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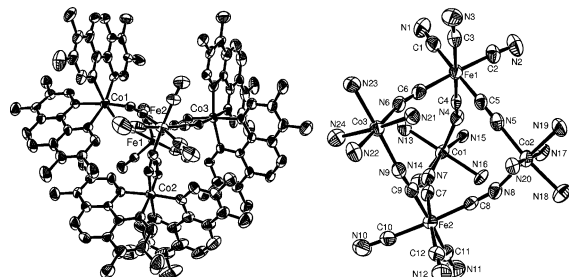
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Research in transition-metal cyanide chemistry[1] is currently experiencing a renaissance due to the novel magnetic properties[2−4] exhibited by face-centered 3-D "Prussian blue" compounds. The chemistry of metal cyanides entered a new phase in recent years with the discovery of low-dimensional cyanide arrays from metal complexes whose ligand environment precludes the formation of an extended face-centered cubic structure. A variety of high-nuclearity cyanide-bridged clusters that have been recently reported exhibit large total spin ground states.[5−7] Among these clusters and arrays, only a few examples incorporate Co and Fe ions because they typically adopt low-spin (LS) electronic configurations.[8−11] Herein, we report the unexpected observation of a charge-transfer-induced spin transition (CTIST)[12] in the molecule, {[Co(tmphen)₂]₃-[Fe(CN)₆]₂} (**1**) (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline). We have found that the structural and physical properties of this discrete μ-CN⁻ cluster are exquisitely sensitive to environmental conditions, thereby causing the metal sites to adopt one of the following oxidation state configurations:

$$\{Co^{II}Co^{III}_2Fe^{II}_2\} \qquad \{Co^{II}_2Co^{III}Fe^{II}Fe^{III}\} \qquad \{Co^{II}_3Fe^{III}_2\}$$
$$\textbf{1a} \qquad\qquad\qquad \textbf{1b} \qquad\qquad\qquad \textbf{1c}$$
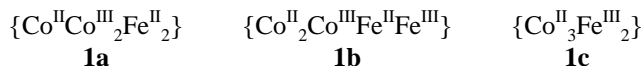
The reaction of [Fe(CN)₆]³⁻ and {Co(tmphen)₂}²⁺ in acetonitrile (MeCN) leads to red crystals of **1**·xH₂O.[13] X-ray data collected for these crystals at $T = 220(2)$ K ($x = 9$)[14] and $T = 110(2)$ K ($x = 13$)[15] reveal virtually identical unit cell parameters.[16] The geometry of the Co₃Fe₂ core for **1** at both temperatures is trigonal bipyramidal, with the three {Co(tmphen)₂} units situated in the equatorial plane of the bipyramid connected to two apical {Fe(CN)₆} units through the N-end of three *fac* CN⁻ ligands (Figure 1). The three {Co-(tmphen)₂} units within the cluster exhibit identical chiralities (all Λ or all Δ), but both homochiral enantiomers of the neutral molecule are present in the crystal as evidenced by the centrosymmetric space group, $P2_1/c$.

The overall geometry of the cluster and the Fe−C bond lengths are virtually the same at the two temperatures, but significant differences are observed in the Co−N bond distances. The Co−N$_{tmphen}$ bond lengths range from 2.103(7) to 2.177(7) Å at 220 K for all three Co centers, in accord with the presence of high-spin (HS) Co^{II} ions.[8;17] At 110 K, the Co(1)−N$_{tmphen}$ bond distances remain unaffected (2.136(7)−2.180(7) Å), whereas the Co−N$_{tmphen}$ distances for the Co(2) and Co(3) centers are significantly shorter (1.978(9)−2.034(7) Å). These metrical parameters indicate that the Co(2) and Co(3) centers undergo a temperature-induced electronic transformation.

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Figure 1. **1** drawn at the 50% probability level ($T = 110$ K). For the sake of clarity, H atoms have been omitted in the figure on the left, and C and H atoms of tmphen have been omitted in the figure on the right.
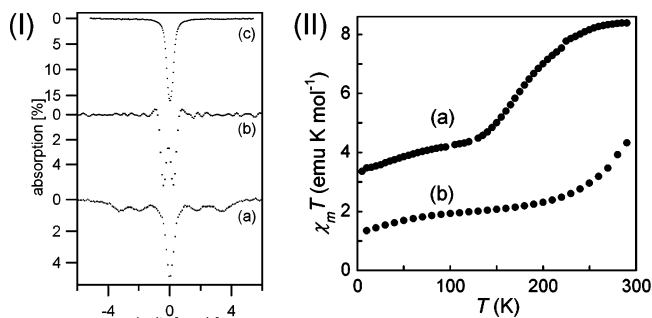
Figure 2. (I) ⁵⁷Fe Mössbauer spectra for the red crystals at (a) 4.2 K and (b) 220 K; the blue solid at (c) 4.2 K. (II) Plot of $\chi_m T$ versus T for the (a) red crystals and (b) blue solid ($H = 1000$ G).

The X-ray data are consistent with the two distinct Co sites going from LS Co^{III} at 110 K to HS Co^{II} at 220 K,[8−11,17] a process which requires the concomitant oxidation of the Fe centers to preserve the neutral charge for **1**. Because it is difficult to elucidate the oxidation state of the Fe centers using X-ray data due to the insensitivity of Fe−C bond distances in [Fe(CN)₆]$^{n-}$ ($n = 3,4$) compounds,[8−10,18,19] ⁵⁷Fe Mössbauer spectroscopy was employed to verify if the transition at the Co centers is indeed accompanied by electron transfer between the Co and Fe sites. The 4.2 K Mössbauer spectrum for a sample of red crystals of **1** suspended in MeCN (to preclude changes in the amount of solvent in the crystals) reveals a line characteristic of LS Fe^{II} (isomer shift $\delta = 0.02$ mm/s relative to Fe metal at 293 K[20]) superimposed on paramagnetic features attributed to LS Fe^{III} (Figure 2I, a). The relative ratio of the absorbance for the two Fe forms is best evaluated as a 1:1 mixture of LS Fe^{II} and LS Fe^{III}.[21] No change in the ratio between the two types of iron is observed up to 110 K. The spectrum of the same sample recorded at 220 K reveals one quadrupole doublet. A Fourier transform procedure was applied to this spectrum to remove the line width of the ⁵⁷Co source.[22] The transformed spectrum (Figure 2I, b) did not reveal any contribution
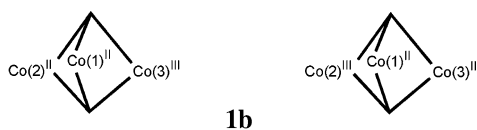
Scheme 1

Co(2)^{II} — Co(1)^{II} — Co(3)^{III}

Co(2)^{III} — Co(1)^{II} — Co(3)^{II}

1b

Scheme 2

Co(2)^{III} — Co(1)^{II} — Co(3)^{III}

Co(2)^{II} — Co(1)^{II} — Co(3)^{II}

1a   **1c**

from LS Fe^{II}. The Mössbauer parameters obtained from the transformed spectrum, $\delta = -0.08$ mm/s and quadrupole splitting $\Delta E_Q = 0.61$ mm/s, are typical for LS Fe^{III}.[20] Mössbauer spectroscopy therefore indicates that the LS Fe^{II} sites present at low temperature are oxidized to LS Fe^{III} with increasing temperature.

To further elucidate the electronic structure of the red crystals of **1**, an analysis of the magnetic properties was carried out on a sample of the crystals suspended in MeCN. The $\chi_m T$ product for these crystals is 8.3 emu K mol^{-1} at room temperature (Figure 2II, a), indicating the presence of three HS Co^{II} ($S = {}^{3}/_{2}$) and two LS Fe^{III} ions ($S = {}^{1}/_{2}$) with significant orbital contributions (spin-only value is 6.375 emu K mol^{-1}). The $\chi_m T$ product for the red crystals decreases to 4.4 emu K mol^{-1} at 130 K, and then exhibits a more gradual decrease to 3.3 emu K mol^{-1} at 2 K. The susceptibility below 130 K is in excellent agreement with the formulation of {Co$^{II}_2$Co^{III}Fe^{II}Fe^{III}} (**1b**), thereby providing incontrovertible evidence that **1** undergoes a CTIST as a function of temperature.

The Mössbauer and magnetic data taken together are in accord with **1b** being the dominant form at low temperatures ($T < 130$ K). The relatively shorter Co–N bond distances determined by X-ray crystallography at $T = 110$ K are therefore a consequence of static disorder due to the superposition of LS Co^{III} and HS Co^{II} ions at the Co(2) and Co(3) sites (Scheme 1). The second possibility is that, at $T < 130$ K, there is an equimolar mixture of **1a** and **1c**, and that the clusters **1a** in this mixture undergo a transition to form **1c** with increasing temperature. In this case, the observed shorter Co–N bond lengths at the two Co sites are a result of disorder of clusters **1a** and **1c** in the crystal lattice (Scheme 2). Although it is difficult to distinguish between these two scenarios experimentally, both situations are entirely consistent with the fact that the red crystals exhibit a CTIST from **1a** or **1b** to **1c** with increasing temperature.

Exposure of the red crystals of **1** to a humid atmosphere produces a blue solid phase for which structural data could not be obtained.[23] The Mössbauer spectrum of this solid at 4.2 K consists of a line with $\delta = 0.02$ mm/s, a value typical of LS Fe^{II} (Figure 2I, c).[20] A high field (7 T) 4.2 K Mössbauer spectrum confirmed the presence of only diamagnetic Fe centers (Supporting Information).[24] The 293 K spectrum of the solid shows also a single line typical of LS Fe^{II}, but, due to comparable isomer shifts for LS Fe^{II} and LS Fe^{III} ions with CN$^-$ coordination, we cannot rule out the presence of up to 25% LS Fe^{III} in this material. The $\chi_m T$ product for the blue solid (~ 2.0 emu K mol^{-1} at 130 K) in the 2–200 K temperature range (Figure 2II, b) is consistent with the presence of a single paramagnetic HS Co^{II} ion in **1**. This indicates that the cluster in the blue phase is best formulated as **1a**. Above 200 K, $\chi_m T$ gradually increases to 4.32 emu K mol^{-1} at 300 K. This increase is not consistent with the paramagnetic behavior of a single HS Co^{II} ion and is attributed to the onset of a CTIST from **1a** to **1b** and/or **1c**.

This study reports an unprecedented CTIST that occurs in cluster **1**, a phenomenon previously observed only in infinite 3-D Co/Fe Prussian blue analogues.[4,12] The properties of this cluster, which exists in three electronic isomeric forms, are exquisitely sensitive to interstitial solvent content as well as temperature. This dependence is under investigation as is the possibility of inducing the spin transition using pressure or light.

Supporting Information Available: Crystallographic files in CIF format, synthesis, elemental analyses, and details of crystallographic, Mössbauer, and magnetic measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) The synthesis of **1** is available in the Supporting Information.
(14) {[Co(tmphen)$_2$]$_3$[Fe(CN)$_6$]$_2$}(**1**)·9H$_2$O: C$_{108}$H$_{114}$Co$_3$Fe$_2$N$_{24}$O$_9$, M_w = 2181, monoclinic, $P2_1/c$, a = 19.261(4) Å, b = 24.123(5) Å, c = 24.782(5) Å, β = 97.74(3)°, V = 11883(4) Å^3, Z = 4, T = 220(2) K, ρ_{calc} = 1.209 g/cm^{-3}, μ = 0.709 mm^{-1}, $F(000)$ = 4468, 38 768 measured reflections, 12 433 unique reflections, λ = 0.71073 Å, 1379 parameters for 12 433 independent reflections with $I > 4\sigma(I)$ gave R1 = 0.0765, wR2 = 0.2234.
(15) {[Co(tmphen)$_2$]$_3$[Fe(CN)$_6$]$_2$}(**1**)·13H$_2$O: C$_{108}$H$_{122}$Co$_3$Fe$_2$N$_{24}$O$_{13}$, M_w = 2253, monoclinic, $P2_1/c$, a = 19.02(1) Å, b = 25.03(2) Å, c = 24.65(2) Å, β = 97.86(2)°, V = 11626(15) Å^3, Z = 4, T = 110(2) K, ρ_{calc} = 1.272 g/cm^{-3}, μ = 0.728 mm^{-1}, $F(000)$ = 4576, 45 873 measured reflections, 12 158 unique reflections, λ = 0.71073 Å, 1399 parameters for 12 158 independent reflections with $I > 4\sigma(I)$ gave R1 = 0.0760, wR2 = 0.2058.
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(23) Elemental analysis of the blue material supports the formulation **1**·24H$_2$O.
(24) The isomer shift of this line coincides with that observed for 50% of the iron in red crystals of **1** at 4.2 K, further supporting our assignment to LS Fe^{II}.

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