Research in transition-metal cyanide chemistry is currently experiencing a renaissance due to the novel magnetic properties 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. Herein, we report the unexpected observation of a charge-transfer-induced spin transition in the discrete cyanide-bridged complex \([\{\text{Co(tmphen)}_2\}_3[\text{Fe(CN)}_6]_2\]}

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Figure 1. 1 drawn at the 50% probability level \((T = 110 \, \text{K})\). 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) \(^{57}\text{Fe}\) 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 \(\Delta\) versus \(T\) for the (a) red crystals and (b) blue solid \((\Delta = 1000 \, \text{G})\).

The X-ray data are consistent with the two distinct Co sites going from LS Co\(^{III}\) at 110 K to HS Co\(^{III}\) at 220 K,\(^8-11,17\) a process which requires the concomitant oxidation of the Fe centers to preserve the neutral charge for I. 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)]\(^{6-}\) (\(n = 3,4\)) compounds,\(^8-10,18,19\) \(^{57}\text{Fe}\) 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 I suspended in MeCN (to preclude changes in the amount of solvent in the crystals) reveals a line characteristic of LS Fe\(^{III}\) (isomer shift \(\delta = 0.02 \, \text{mm/s relative to Fe metal at 293 K}\) \(^{20}\) ) 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 \(^{57}\text{Co}\) source.\(^{22}\) The transformed spectrum (Figure 2I, b) did not reveal any contribution

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from LS Fe\textsuperscript{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\textsuperscript{III}.\textsuperscript{20} Mössbauer spectroscopy therefore indicates that the LS Fe\textsuperscript{II} sites present at low temperature is oxidized to LS Fe\textsuperscript{III} with increasing temperature.

To further elucidate the electronic structure of the red crystals of \textbf{I}, an analysis of the magnetic properties was carried out on a sample of the crystals suspended in MeCN. The $\gamma_{T}T$ product for these crystals is 8.3 emu K mol$^{-1}$ at room temperature (Figure 2II, a), indicating the presence of three HS Co\textsuperscript{II} ($S = \frac{3}{2}$) and two LS Fe\textsuperscript{III} ions ($S = \frac{3}{2}$) with significant orbital contributions (spin-only value is 6.375 emu K mol$^{-1}$). The $\gamma_{T}T$ 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 $\{Co\textsubscript{II}\text{Fe}^{III}\text{Fe}^{III}\}$ (1b), thereby providing incontrovertible evidence that \textbf{I} 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$-\overline{N}$ 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\textsuperscript{III} and HS Co\textsuperscript{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 1c with increasing temperature. In this case, the observed shorter Co$-\overline{N}$ 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 \textbf{I} to a humid atmosphere produces a blue solid phase for which structural data could not be obtained.\textsuperscript{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\textsuperscript{II} (Figure 2I, c).\textsuperscript{20} A high field (7 T) 4.2 K Mössbauer spectrum confirmed the presence of only diamagnetic Fe centers (Supporting Information).\textsuperscript{24} The 293 K spectrum of the solid shows also a single line typical of LS Fe\textsuperscript{II}, but, due to comparable isomer shifts for LS Fe\textsuperscript{II} and LS Fe\textsuperscript{III} ions with CN$^{-}$ coordination, we cannot rule out the presence of up to 25% LS Fe\textsuperscript{III} in this material. The $\gamma_{T}T$ product for the blue solid ($\sim 2.0$ 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\textsuperscript{II} ion in \textbf{I}. This indicates that the cluster in the blue phase is best formulated as 1a. Above 200 K, $\gamma_{T}T$ 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\textsuperscript{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 \textbf{I}, a phenomenon previously observed only in infinite 3-D Co/Fe

**References**

(13) The synthesis of $I$ is available in the Supporting Information.