Spin Transitions

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An Unprecedented Charge Transfer Induced Spin Transition in an Fe–Os Cluster**

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The study of paramagnetic cyanide compounds is one of the most active research areas in the field of coordination chemistry.[1] Remarkable properties have been documented for both molecules and extended phases, including high-temperature magnetic ordering,[2] single-molecule magnetism,[3–5] single-chain magnetism,[6] photomagnetism,[7,8] spin crossover (SCO),[9,10] and a less common phenomenon known as charge transfer induced spin transition (CTIST).[11–13] The CTIST process involves formal intramolecular electron transfer with concomitant spin-state changes at the metal centers and can be induced by light irradiation or changes in temperature. This two-state magnetic and optical accessibility is crucial for implementation of molecule-based materials in technological devices,[14] a fact that accounts for the strong interest in these compounds.

The first report of a cyanide compound that exhibits CTIST properties is from the group of Hashimoto, who reported that films of the Prussian Blue (PB) analogue $K_{0.2}Co_{1.4}\{Fe(CN)_6\}\cdot 6.9\,H_2O$ exposed to red light undergo an increase in both the ferrimagnetic ordering temperature from 16 K to 19 K and the magnetization.[8] The effect is fully thermally reversible and partially reversed by illumination with blue light. Additional materials that exhibit CTIST are the PB phase $Rb_{0.88}Mn[Fe(CN)_6]_{0.96}\cdot 0.5\,H_2O$[15] and more exotic materials with 5d metal ions such as $Co^{II}_3[W^{V}(CN)_8]_2(pyrimidine)_4\cdot 6\,H_2O$.[12]

The aforementioned exciting developments in PB chemistry prompted us to investigate the properties of cyanide-bridged heterometallic clusters known to undergo facile electron transfer through the $M{-}C{\equiv}N{-}M'$ linkage. These efforts led to the first documented case of CTIST in a molecule-based Fe/Co material, namely $\{[Co(tmphen)_2]_3[Fe(CN)_6]_2\}\cdot x\,H_2O$ (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline), which is a member of a large family of related trigonal bipyramidal (TBP) clusters. In these clusters, two axial $[M(CN)_6]^{3-}$ ions form bridges to three equatorially disposed $[M'(tmphen)_2]^{2+}$ groups.[16] We discovered that the $\{[Co(tmphen)_2]_3[Fe(CN)_6]_2\}$ cluster from this family is quite remarkable in that it can exist in different electronic isomeric forms, fir example, $\{Co^{III}_2Co^{II}Fe^{II}_2\}$ and $\{Co^{II}_3Fe^{III}_2\}$.[11] More recently, the cyanide-bridged cube $\{[(pzTp)Fe^{III}(CN)_3]_4[Co^{II}(pz)_3CCH_2OH]_4[ClO_4]_4\}$ (pzTp = tetrakis(1*H*-pyrazol-1-yl)borato) was found to undergo a sharp CTIST at 250 K.[7]

Herein we report an unprecedented CTIST for the new heterobimetallic cluster $\{[Fe(tmphen)_2]_3[Os(CN)_6]_2\}$ (**1**), which contains only Group 8 metal ions. Full characterization by structural, magnetic, and spectroscopic methods points to a reversible transition between the $Fe^{II}{-}N{\equiv}C{-}Os^{III}$ and $Fe^{III}{-}N{\equiv}C{-}Os^{II}$ redox pairs. Most importantly, the iron centers switch between low-spin (LS) Fe^{II} and high-spin (HS) Fe^{III}, respectively, a type of transition that has not been previously observed for Fe ions to our knowledge.

The reaction of $[PPN]_3[Os(CN)_6]$ (PPN = bis(triphenylphosphine)iminium)) and in situ produced $[Fe(tmphen)_2]^{2+}$ in acetonitrile leads to the formation of **1**, which crystallizes in the centrosymmetric space group $P2_1/c$ as found for related TBP molecules (Figure 1).[16,17]

The crystallographic data for **1** reveal that the average Fe–N(tmphen) bond length increases by 0.09–0.2 Å between 110

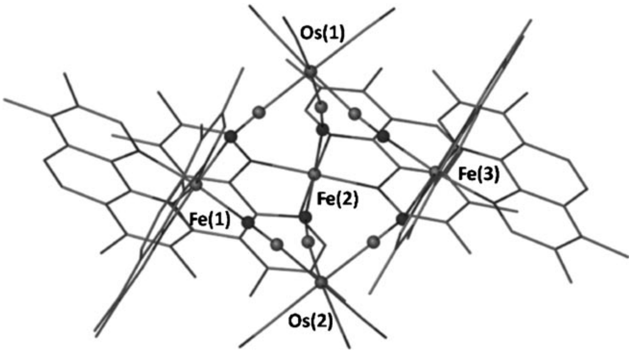

Figure 1. Molecular structure of **1** from X-ray coordinates at 110 K. Hydrogen atoms are omitted for clarity.

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and 300 K, an indication that a change in the oxidation and/or spin states of these metal ions is occurring (Tables 1 and S1 in the Supporting Information). A large (ca. 0.2 Å) increase in the Fe–N bond length is typically observed for the transformation between LS and HS configurations for Fe^{II} spin crossover complexes.[18] We have observed such a SCO transition for two of the three equatorial Fe sites in the $\{[Fe(tmphen)_2]_3[Fe(CN)_6]_2\}$ and $\{[Fe(tmphen)_2]_3[Co(CN)_6]_2\}$ clusters (the labeling scheme is such that Fe(1) and Fe(3) are SCO sites but Fe(2) is not). Similarly, the increase in Fe–N(tmphen) bond lengths for the Fe(1) and Fe(3) centers of the $\{[Fe(tmphen)_2]_3[Os(CN)_6]_2\}$ cluster is larger than that of the Fe(2) site. This difference may be due to weak intra- and intermolecular interactions,[16] most likely related to the packing of the clusters into dimer units. In the dimers, there are π contacts between the tmphen ligands of Fe(1) and Fe(3) of the $\{[Fe(tmphen)_2]_3[Os(CN)_6]_2\}$ cluster but not between the ligands of Fe(2) (Figure S1). While the changes in the average Fe–N bond lengths are compatible with a LS Fe^{II} to HS Fe^{II} change, we cannot rule out that the change is due to a transition from LS Fe^{II} to HS Fe^{III}. We could not find a benchmark for the change in bond length that accompanies a transition from LS Fe^{II} to HS Fe^{III}, because a search of the Cambridge Structural Database revealed that there is no structurally characterized example of a HS Fe^{III} complex with four imine and two N-coordinated cyanide or thiocyanide ligands.[19,20] Therefore, the X-ray data indicate that the metal core in **1** is $\{(LS\text{-}Fe^{II})_3Os^{III}{}_2\}$ at low temperature and that two of the three iron sites of the cluster become HS Fe^{II} or HS Fe^{III} at 350 K. The 4.2 K EPR spectrum of **1** exhibits a signal characteristic of LS Os^{III} ($S = 1/2$), which corroborates the $\{Fe^{II}{}_3Os^{III}{}_2\}$ valence assignment for the cluster at low temperature (inset in Figure 2).

Table 1: Average Fe–N(tmphen) bond lengths [Å] for **1**.

T [K]	Fe(1)	Fe(2)	Fe(3)
300	2.16(1)	2.05(1)	2.17(1)
110	1.99(1)	1.96(1)	1.99(1)

Variable-temperature magnetic susceptibility measurements in an applied dc field of 0.1 T for a polycrystalline sample of **1** showed an abrupt decrease in χT from 9.37 emu K mol^{-1} at 350 K to 2.13 emu K mol^{-1} at 220 K, followed by a slow decrease to 1.2 emu K mol^{-1} at 50 K (Figure 2). The approximately 7.3 emu K mol^{-1} change in χT between 350 and 200 K is indicative of a gradual change in the spin state at the metal ions due to either SCO or CTIST. Specifically, the change in χT could be due to a LS to HS Fe^{II} transition with 47 % and 80 % of the Fe sites of the cluster becoming HS Fe^{II} at 300 K and 350 K, respectively, or to a CTIST from $\{LS\text{-}Fe^{II}\text{–}N{\equiv}C\text{–}Os^{III}\}$ to $\{HS\text{-}Fe^{III}\text{–}N{\equiv}C\text{–}Os^{II}\}$ with 35 % and 60 % of the Fe sites becoming HS Fe^{III} at 300 K and 350 K, respectively.

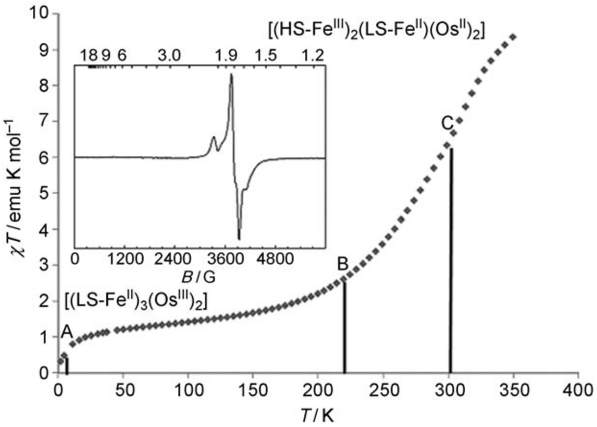

Figure 2. Plot of χT for a polycrystalline sample of **1** measured in an applied magnetic field of 0.1 T. Lines marked A, B, C identify the temperatures at which Mössbauer measurements were made. Inset: X-band EPR spectrum of a powder sample of **1**. An average g value of 1.9 was observed for Os^{III} in the cluster. Experimental conditions: $T = 2.0$ K; microwave frequency 9.63 GHz; microwave power 317 μW; modulation amplitude 10 G.

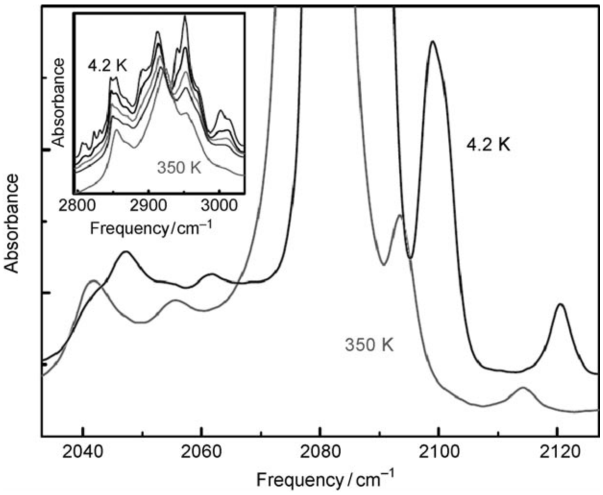

Figure 3. Infrared spectra of a crystalline sample of **1** are characteristic for cyanide complexes, with terminal modes being at lower frequencies and bridging modes at higher frequencies. The inset displays a close-up view of the C–H stretch at 4.2, 110, 190, 250, and 350 K.

Variable-temperature infrared spectra of **1** (Figure 3) show a strengthening of the C–N bond with decreasing temperature, reflected in the shift of the ν(CN) vibrational modes to higher frequencies. This observation can be compared with predicted trends for our two SCO transition and CTIST working models. In a typical HS Fe^{II} to LS Fe^{II} transition, the bridging cyanide modes are expected to change only slightly, and the terminal stretches of $[Os^{III}(CN)_6]^{3-}$ would be affected even less. In contrast, if the transition involves a change in transition-metal oxidation state such as between $[(LS\text{-}Fe^{II})(HS\text{-}Fe^{III})_2(Os^{II})_2]$ and $[(LS\text{-}Fe^{II})_3(Os^{III})_2]$ at high and low temperature, respectively, both bridging and terminal cyanide stretching modes would be affected. For the latter case, it can also be anticipated that the low-temperature infrared data would reflect the higher oxidation of Os centers, resulting in higher-frequency stretches. As mentioned above, with decreasing temperature, we observe a systematic "hardening" of all ν(CN) modes and an overall increase in oscillator strength, which indicates that a CTIST and not a HS Fe^{II} to LS Fe^{II} SCO transition takes place in $\{[Fe(tmphen)_2]_3[Os(CN)_6]_2\}$. However, we note that the observed hardening of the ν(CN) modes (5–6 cm^{-1}) is much smaller than that expected for the CTIST in isolation (Table S3).[8,11] This difference may be related to the presence of competing CH···N≡C hydrogen-bonding-like interactions in this material, which tend to counteract the hardening effect induced by lowering the temperature (inset Figure 3). The lack of any CN stretches at intermediate temperatures distinct from those observed at 4.2 K and 350 K suggests that the transition is from $[Fe^{II}_3Os^{III}_2]$ directly to $[Fe^{III}_2Fe^{II}Os^{II}_2]$ and not through the $[Fe^{II}_2Fe^{III}Os^{III}Os^{II}]$ form of the cluster.

To directly investigate the oxidation and spin state of the Fe ions in **1**, ^{57}Fe Mössbauer spectra were obtained at temperatures between 4.2 and 300 K and in applied magnetic fields of up to 8 T. The Mössbauer parameters for **1** are summarized in Table 2. The dominant feature of the 4.2 K spectrum (Figure 4) is a quadrupole doublet with an isomer shift δ of 0.40 $mm\,s^{-1}$ and a quadrupole splitting ΔE_Q of 0.36 $mm\,s^{-1}$; this doublet represents more than 85 % of the Fe in the sample (red line in Figure 4a). The δ and ΔE_Q parameters are characteristic of LS Fe^{II}. A spectrum obtained at 4.2 K and 8 T for the same sample confirmed that the majority of the iron in the sample is diamagnetic LS Fe^{II}.

Now we turn to the scenario that a LS Fe^{II} to HS Fe^{II} transition takes place in **1**. In this case, the Mössbauer spectra obtained at 220 K and 300 K would show a quadrupole doublet with $\delta \approx 1\ mm\,s^{-1}$ and $\Delta E_Q \approx 3\ mm\,s^{-1}$ and whose right line would be most easily discernible at greater than 2 $mm\,s^{-1}$ (Figure 4d). The absence of a feature in this region of the 300 K spectrum excludes the possibility of a SCO event at the iron centers. On the other hand, if HS Fe^{III} forms by electron transfer between the Fe and Os ions through CTIST, the HS Fe^{III} would be represented in the Mössbauer spectra at $T \geq 220$ K by a quadrupole doublet that would be visible as a shoulder on the right side of the doublet for LS Fe^{II}. Indeed, such a spectral feature is observed in the 220 and 300 K spectra (blue line in Figure 4b,c). The change in the relative contribution of HS Fe^{III} to the spectrum measured at 300 K is in good agreement with the change estimated on the basis of the magnetic susceptibility data (Table 2 and above). Therefore the Mössbauer data are consistent with a CTIST event that interconverts LS Fe^{II}–C≡N–Os^{III} and HS Fe^{III}–C≡N–Os^{II}.

Table 2: Mössbauer parameters for a polycrystalline sample of **1**.

T [K]	Fe site	δ [$mm\,s^{-1}$][a]	ΔE_Q [$mm\,s^{-1}$]	Relative contribution [%]
4.2	LS Fe^{II}	0.40	0.36	95
	LS Fe^{II}*	0.28	0.00	5
220	LS Fe^{II}	0.35	0.35	72
	HS Fe^{III}	0.54	0.55	22
	LS Fe^{II}*	0.28	0.00	6
300	LS Fe^{II}	0.32	0.28	66
	HS Fe^{III}	0.50	0.55	27
	LS Fe^{II}*	0.28	0.00	6

[a] Isomer shift determined with respect to Fe metal at room temperature. The standard deviations are 0.01 for δ, 0.02 for ΔE_Q, and 2 for relative contribution.

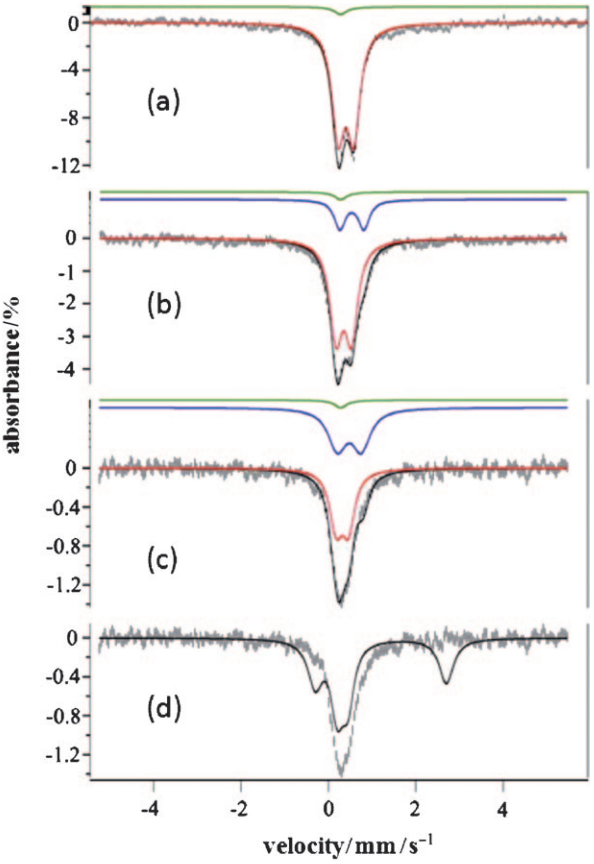

Figure 4. Mössbauer spectra obtained at a) 4.2 K, b) 220 K and c) 300 K. The plot in (d) represents a simulation of HS Fe^{II} at 300 K. The red trace is the simulated contribution of LS Fe^{II}, the blue line is HS Fe^{III}, and the green line represents a LS Fe^{II} impurity. The black line represents the sum of contributions for all types of Fe in the sample.

The slight asymmetry of the quadrupole doublet observed in the 4.2 K Mössbauer spectrum reflects the presence of a small amount of LS Fe^{II} with Mössbauer parameters that are different from those of the majority LS Fe^{II} species. This type of Fe^{II} ion represents at most 5 % of the Fe in the sample (Figure 4a and S2a, LS Fe^{II}* Table 2). The spectrum obtained at 4.2 K and 8 T for the same sample revealed that the sample also contains up to 10 % HS Fe^{III} (Figure S3). Several synthetic batches showed these minority LS Fe^{II}* and HS Fe^{III} features at 4.2 K (Figure S2 and Table S2). These ions likely originate from a population of less than 10 % clusters that contain “locked” HS Fe^{III}–C≡N–Os^{II} units at 4.2 K. The presence of these minority clusters at low temperature also explains the χT value of 1.5 $emu\,K\,mol^{-1}$ found for the sample of **1** at 50–100 K.

In summary, we have investigated the new cyanide-bridged $\{[Fe(tmphen)_2]_3[Os(CN)_6]_2\}$ cluster by structural, spectroscopic, and magnetic methods. To our knowledge, the compound is only the second example of cluster that contains the hexacyanoosmate(III) anion as a building block, and it constitutes the first example in which a HS Fe^{III} ion is in a coordination environment of four imine nitrogens and two N-coordinated cyanides. Most importantly, our studies revealed an unprecedented type of reversible, temperature-induced CTIST centered at room temperature from LS Fe^{II}–Os^{III} to HS Fe^{III}–Os^{II}. These intriguing results represent a valuable addition to the relatively small body of literature on CTIST phenomenon.

Experimental Section

$FeCl_2$ (0.052 g, 0.413 mmol) and tmphen (0.216 mg, 0.914 mmol) were combined in acetonitrile (80 mL). The solution was stirred for 30 min in an inert N_2 atmosphere dry box. The resulting dark red solution was combined with a solution of $(PPN)_3[Os(CN)_6]$ (0.659 g, 0.336 mmol) in acetonitrile (80 mL). This solution was left undisturbed for 4–5 days after which time a crop of purple-red crystals was collected by filtration and washed with acetonitrile (3 × 30 mL). Yield 118 mg (31 %). Elemental analysis and TGA indicated the presence of interstitial water molecules ($9\,H_2O$), which is common for these materials. Calcd. for $C_{108}H_{114}Fe_3N_{24}O_9Os_2\cdot 9\,H_2O$: O 5.89, N 13.76, C 53.08, H 4.70; found: O 5.98, N 13.89, C 53.64, H 4.85 %.

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