Inorganic Chemistry
ARTICLE
pubs.acs.org/IC

Light-Induced Excited Spin State Trapping and Charge Transfer in Trigonal Bipyramidal Cyanide-Bridged Complexes

Kristen E. Funck,[†] Andrey V. Prosvirin,[†] Corine Mathonière,*[,‡] Rodolphe Clérac,*[,§,∥] and Kim R. Dunbar*[,†]

[†]Department of Chemistry, Texas A&M University, College Station, Texas 77842, United States

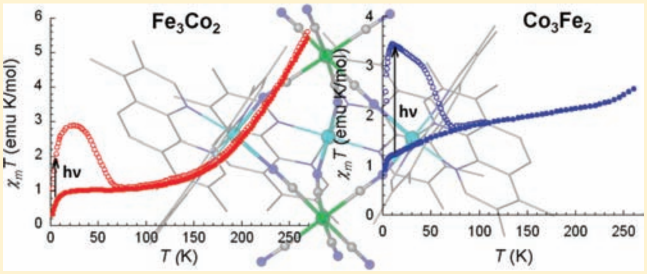
[‡]CNRS, Université de Bordeaux, ICMCB, Groupe des Sciences Moléculaires, 87 Avenue du Dr. Albert Schweitzer, F-33608 Pessac, France

[§]CNRS, UPR 8641, Centre de Recherche Paul Pascal (CRPP), Equipe "Matériaux Moléculaires Magnétiques" 115 Avenue du Dr. Albert Schweitzer, F-33600 Pessac, France

[∥]Université de Bordeaux, UPR 8641, F-33600 Pessac, France

Supporting Information

ABSTRACT: Three members of the family of trigonal bipyramidal (TBP) complexes of general formula $[M(tmphen)_2]_3[M'(CN)_6]_2$ (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline) or $[M_3M'_2]$, which are known to exhibit thermally induced spin crossover and charge transfer, have been investigated for optical and photomagnetic properties. The light-induced excited spin-state trapping (LIESST) effect found in classical spin crossover compounds, such as $[Fe(phen)_2(NCS)_2]$, was explored for the $[Fe_3Fe_2]$ and $[Fe_3Co_2]$ compounds. Similarly, inspired by the light-induced charge-transfer properties of $K_{0.2}Co_{1.4}[Fe(CN)_6]\cdot 6.9H_2O$ and related Prussian blue materials, the possibility of photo-induced magnetic changes was investigated for the $[Co_3Fe_2]$ TBP complex. Optical reflectivity and magnetic susceptibility measurements were used to evaluate the photoactivity of these compounds. A comparison of these data before and after light irradiation demonstrates that (i) the spin crossover of the Fe^{II} centers in the $[Fe_3Fe_2]$ and $[Fe_3Co_2]$ analogues and the (ii) charge transfer events in the $[Co_3Fe_2]$ complex occur with temperature and irradiation. In addition, photomagnetic behavior is exhibited by all three compounds. The photoconversion efficiency has been estimated at 20% of photo-induced high spin Fe^{II} centers in $[Fe_3Co_2]$, 30% of paramagnetic $Co^{II}-Fe^{III}$ pairs in $[Co_3Fe_2]$, and less than 2% of photo-induced high spin Fe^{II} centers in $[Fe_3Fe_2]$.



INTRODUCTION

Cyanide chemistry is a forefront topic in molecular magnetism owing largely to the discovery of Prussian blue (PB) analogues that exhibit magnetic ordering at high temperatures.[1−3] These fascinating materials have also found use as hydrogen storage materials,[4,5] molecular sieves,[6] and antidotes for radioactive poisoning.[7] As a natural extension of the PB framework solids, chemists have turned to the building block or modular approach[8,9] to design cyanide aggregates of a desired geometry. The premise of this method is to limit the growth of a material to a finite size by the use of transition metal complexes in which some of the coordination sites are blocked by multidentate ligands. This highly successful strategy has produced many new cyanide-bridged molecules with interesting properties including single-molecule magnet behavior, spin crossover, cyanide linkage isomerism, and rich redox chemistry.[9] Another intriguing property exhibited by cyanide compounds is photomagnetism, which allows for the control of the magnetic properties with light irradiation. Although photomagnetic effects are known to trigger a variety of events including spin crossover, metal-to-metal charge transfer, ligand-to-metal charge transfer, cis/trans isomerism, or cyclization, the spin crossover (light-induced excited spin state trapping or LIESST) and charge transfer phenomena are the most common.[10,11] Photo-induced spin crossover was first observed in 1982 on a nanosecond time scale by McGarvey and Lawthers for three mononuclear Fe^{II} complexes.[12] In 1984, Decurtins and Gütlich et al., demonstrated that the high spin (HS) state of $[Fe(ptz)_6](BF_4)_2$ (ptz =1-propyl-tetrazole) could be trapped at low temperature upon irradiation with green light, a phenomenon that was dubbed LIESST (light-induced excited spin state trapping).[13] Since this discovery, LIESST has been observed for many spin-crossover compounds, including numerous $[Fe(diimine)_2(NCX)_2]$ complexes (X = S, Se).[14−21] Photo-induced charge-transfer was first observed in 1996 by Sato et al. in the Prussian blue analogue $K_{0.2}Co_{1.4}[Fe(CN)_6]\cdot 6.9H_2O$.[22] Under red light irradiation (660 nm) and at low temperatures (<20 K), this material exhibits a conversion of its paramagnetic ground state to a photo-induced ferrimagnetic ordered phase. Remarkably, the reverse process is possible using blue light irradiation (at 450 nm). Several studies have been devoted to

Received: September 7, 2010
Published: March 10, 2011

Co/Fe Prussian Blue networks, and today the mechanism of this photo-induced charge-transfer phenomenon is clearly understood. In these materials, the $\mathrm{Co^{III}}_{\mathrm{LS}}$—NC—$\mathrm{Fe^{II}}$ ground state is reversibly converted into a $\mathrm{Co^{II}}_{\mathrm{HS}}$—NC—$\mathrm{Fe^{III}}$ magnetic state using light irradiation or temperature.[23−33]

Although mononuclear species and extended structures with photomagnetic properties are quite prevalent, to date, only a few photomagnetic molecular aggregates have been reported. Several compounds containing octacyanometallate anions have been synthesized that exhibit a photo-induced MM′CT,[34−40] but only three photomagnetic model compounds based on a Prussian blue analogue, namely the $[\mathrm{Co^{II}}_4\mathrm{Fe^{III}}_4]$ cube[41] and two $[\mathrm{Co^{II}}_2\mathrm{Fe^{III}}_2]$ square molecules have been reported.[42,43] Several dinuclear $\mathrm{Fe^{II}}$ compounds that exhibit the LIESST effect have appeared in the literature as well,[44−54] but only four complexes of higher nuclearity than two have been investigated vis-à-vis their light-induced magnetic properties.[55−58]

The first member of the trigonal bipyramidal cyanide complex family is $[\mathrm{Ni^{II}(bpm)_2}]_3[\mathrm{Fe^{III}(CN)_6}]_2$ (bpm = bis(1-pyrazolyl)-methane), reported in 1997 by Murray and co-workers.[59] In 2003, the Dunbar group reported a similar compound $[\mathrm{Ni^{II}(tmphen)_2}]_3[\mathrm{Fe^{III}(CN)_6}]_2$.[60] Over the past decade, efforts in our laboratories have led to an expansion of this molecular geometry to over twenty examples of compounds of general formula $[\mathrm{M(tmphen)_2}]_3[\mathrm{M'(CN)_6}]_2$ (hereafter denoted as $[\mathrm{M_3M'_2}]$).[61−69] The structure of the molecules consist of two $[\mathrm{M'(CN)_6}]^{3-}$ ions in the axial (apical) positions of the TBP core, each connected by $\mathrm{CN^-}$ ligands to the three equatorial $[\mathrm{M(tmphen)_2}]^{2+}$ moieties.

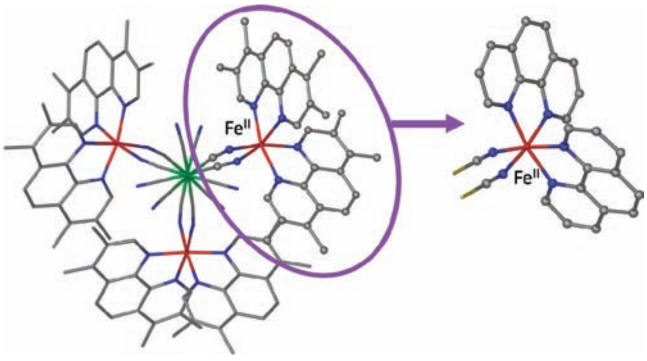


Figure 1. Crystal structure (top view) of the $[\mathrm{Fe_3Co_2}]$ TBP complex with emphasis on the similarity of the equatorial sites to the $[\mathrm{Fe(phen)_2(NCS)_2}]$ molecule (right). Hydrogen atoms are omitted for clarity. Color scheme: red, Fe; green, Co; gray, C; blue, N, yellow, S.

The impetus for our research in this area is to investigate the optical and photomagnetic properties of TBP cyanide molecules that display spin crossover (SCO) phenomena. By employing a combination of magnetic and Mössbauer data, we had documented previously that the $\mathrm{Fe^{II}}$ sites of the $[\mathrm{Fe_3Co_2}]$ and $[\mathrm{Fe_3Fe_2}]$ analogues undergo thermally induced SCO.[65] Given that the first coordination sphere of the equatorial $\mathrm{Fe^{II}}$ ions is similar to that of the classic compound $[\mathrm{Fe(phen)_2(NCS)_2}]$ (phen = 1,10-phenanthroline, Figure 1), we hypothesized that a LIESST effect also would be possible. As for the earlier reported $[\mathrm{Co_3Fe_2}]$ TBP complex,[62,63] which undergoes a charge-transfer induced spin crossover (CTISC), we rationalized that a photo-induced MM′CT akin to the Co/Fe Prussian blue phases should be possible (Figure 2). In the present work, we report the changes in magnetic properties for several of these TBP cyanide molecules after irradiation in the range of the MM′CT band.

■ EXPERIMENTAL SECTION

Syntheses and Characterizations. *Trigonal Bipyramidal Complexes.* The molecules in this study were prepared as previously described.[65,67] The $[\mathrm{Co_3Fe_2}]$ compound (blue solid form) was prepared in air by slowly combining acetonitrile solutions of $(\text{18-C-6-K})_3[\mathrm{Fe(CN)_6}]$ (~8.6 mM), $\mathrm{Co(NO_3)_2\cdot 6H_2O}$ (~6.9 mM), and tmphen (~17.2 mM).[67] The $[\mathrm{Fe_3Fe_2}]$ and $[\mathrm{Fe_3Co_2}]$ samples were prepared in a dry nitrogen atmosphere by combining an acetonitrile solution of $(\mathrm{TBA})_3[\mathrm{Fe(CN)_6}]$ or $(\text{18-C-6-K})_3[\mathrm{Co(CN)_6}]$ (4 mM) with an acetonitrile solution of $\mathrm{FeCl_2}$ (4 mM) and tmphen (8.2 mM).[65] Batches of the compounds were characterized by infrared (IR) spectroscopy and magnetic susceptibility measurements to confirm their identities and purities.

Treatment of $[\mathrm{Co_3Fe_2}]$ for Hydration Study. Crystals of $[\mathrm{Co_3Fe_2}]$, prepared in acetonitrile, were collected by filtration on a fritted filter funnel. Air was pulled by suction through the crystals for approximately 5 min before the sample was collected and then immediately used for the photomagnetic measurements and thermogravimetric analysis (TGA). At the same time, to perform susceptibility calibration of the photomagnetic measurements, a sample was prepared and stored during the photomagnetic studies in a tightly wrapped plastic bag and sealed in a small glass vial to retain the initial solvation level of the crystals; it was measured immediately after the photomagnetic studies. The remaining compound was placed in a vial, exposed to humid air,[70] and covered by a Kimwipe to prevent contamination. On the specified days, samples were successively removed for photomagnetic and TGA measurements, with the remaining sample left to stand in the open vial.

Physical Measurements. The thermogravimetric analyses (TGAs) were performed in the 298−673 K temperature range at a heating rate of 5 K/min on either an Instrument Specialists Incorporated TGA 1000 thermogravimetric analyzer, under an $\mathrm{N_2}$ gas flow of 20 L/min,

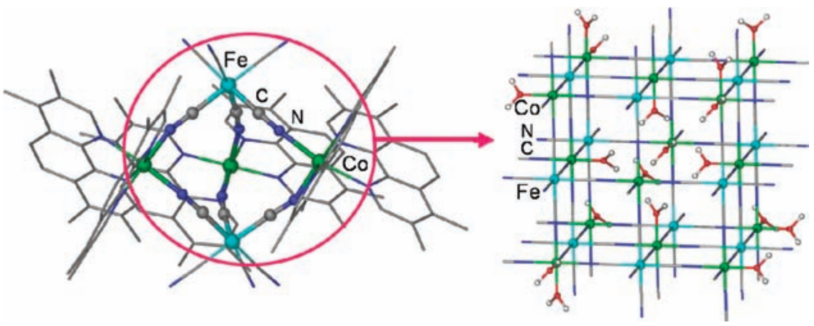


Figure 2. Crystal structure (side view) of the $[\mathrm{Co_3Fe_2}]$ TBP complex with emphasis on the similarity of the TBP core to a Co−Fe Prussian blue material. Hydrogen atoms are omitted from the TBP complex for the sake of clarity. Color scheme: green, Co; light blue, Fe; gray, C; blue, N, red, O.

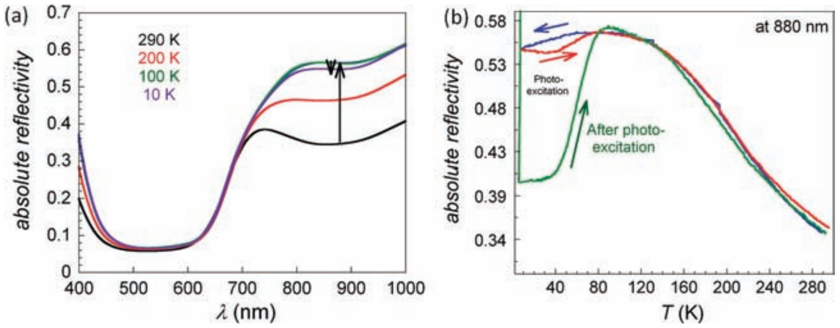


Figure 3. (a) Surface reflectivity spectra of $[Fe_3Co_2]$ under continuous white light irradiation (0.05 mW/cm^2; black, 290 K; red, 200 K; green, 100 K; purple, 10 K). (b) Absolute surface reflectivity at 880 nm (with 0.05 mW/cm^2 white light irradiation) with cooling (blue), heating (red), and heating after 90 min of white light irradiation at 5 K (0.7 mW/cm^2, green).

or on a Shimadzu TGA-50 at 30 L/min. Infrared spectra were measured on a Nicolet 740 FTIR spectrometer as Nujol mulls placed between KBr plates. Diffuse reflectance spectra were measured on a Hitachi U-4100 UV−vis−NIR spectrophotometer with a Praying Mantis diffuse reflection accessory or a Hewlett-Packard 8453 UV−vis spectrophotometer with a Labsphere RSA-HP-8453 reflectance spectroscopy accessory. Surface reflectivity measurements were performed on a home-built system in the 10−300 K range. A tungsten-halogen light source was used (Leica CLS 150 XD, adjustable from 0.0001 to 1 W/cm^2) at wavelengths between 300 and 1000 nm. All measurements were calibrated against a NIST traceable reflectance standard (sphereOptics, ref SG3054). This setup collects the light reflected by the sample (that is the sum of direct and diffuse reflected light). The temperature heating and cooling rates were maintained at 4 K/min.

Magnetic measurements were performed on a Quantum Design SQUID, MPMS-XL magnetometer. Magnetic susceptibility measurements in the direct current (dc) mode were carried out in an applied field of 0.1 T in the 2−300 K range. Magnetic data obtained for samples were corrected for diamagnetic contributions by the use of the Pascal constants.[71] Because of the variable content of solvent in the crystals, each sample was subjected to TGA, and the molecular weight of each compound was adjusted according to the interstitial solvent content determined. Some of the photomagnetic measurements (at Texas A&M University) were obtained using the Quantum Design fiber optic sample holder. Samples (1−3 mg) were sealed in clear tape and placed in a glass tube equipped with an optical fiber placed ~2 mm from the sample. The white light source used was a Thor Laboratories OSL1 High Intensity fiber light source (adjustable up to 0.22 W/cm^2 through a 36″ fiber bundle). Because of the small amount of sample, an applied field of 0.5 T was used. Susceptibility measurements were calibrated to determine sample mass by comparing to a dc measurement of a known larger mass of the same batch of sample. Additional photomagnetic measurements (measured at Centre de Recherche Paul Pascal and Institut de Chimie de la Matière Condensée de Bordeaux, Pessac) were performed using a mixed gas Ar−Kr laser (spectrum physics Beam Lock 2060) coupled through an optical fiber directed into the magnetometer cavity or with the tungsten-halogen light source (Leica CLS 150 XD, adjustable from 0.0001 to 1 W/cm^2). Samples (2−3 mg) were packed into a thermoformed plastic straw placed about 3.5 cm from the fiber. The water content of the samples was determined by TGA (Texas A&M University) before mailing to Pessac in a sealed container and was assumed to remain constant.

RESULTS AND DISCUSSION

Reflectivity and Photomagnetic Studies of $[Fe_3Co_2]$. To test the possibility of photomagnetic properties in the $[Fe_3Co_2]$ compound, we first investigated its optical properties. The room temperature diffuse reflectance spectrum consists of two absorbance bands, one at 880 nm and the second one around 500 nm (Supporting Information, Figure S1). The optical reflectivity spectra were measured to determine the response of the sample to temperature changes and to white light irradiation. Upon cooling a sample under continuous low-power white light irradiation (0.05 mW/cm^2), the spectra revealed two broad bands as already observed in the absorbance spectrum, one centered at 540 nm that exhibited negligible variation with temperature and a second one at 880 nm, noted R_{880} hereafter, that varied greatly with temperature (Figure 3a). There is an increase in R_{880} (i.e., decrease in absorbance) from 295 to 100 K. This change is reminiscent of the gradual spin crossover ($Fe^{II}_{HS} \rightarrow Fe^{II}_{LS}$) that is known to occur in this compound.[65] Further cooling of the sample to 10 K results in a slight decrease in R_{880}, which suggests a LIESST effect (Figure 3b, blue line). To further study this photoexcitation, reflectivity spectra were measured on a sample cooled to 5 K in the dark and then irradiated with a high power light (0.7 mW/cm^2) for 90 min (Supporting Information, Figure S2). R_{880} decreased continuously during the irradiation (i.e., the absorbance increased) such that the spectrum match resembled the room temperature spectrum, suggesting that the photo-conversion on the surface is nearly quantitative. It is worth mentioning that the reflectivity measurements test the surface of the sample, and thus the photo-conversion efficiency at the surface, but the photoactivity of the bulk sample can be significantly different. The 880 nm absorbance band, corresponding to a d-d transition ($^5T_2 \rightarrow {}^5E$) of the HS Fe^{II} ion similar to the 840 nm absorption reported for $[Fe(phen)_2(SCN)_2]$,[72] increases in intensity with both irradiation and increasing temperature. Finally, the temperature dependence of the photo-induced reflectivity at 880 nm reveals three optical changes (Figure 3b, green line): a "stable" reflectivity signal up to 30 K (the photogenerated Fe^{II}_{HS} is trapped at the time scale of the experiment, with a sweeping temperature rate of 4 K/min), a thermal relaxation ($Fe^{II}_{HS} \rightarrow Fe^{II}_{LS}$) from 30 to 80 K, and the known thermally induced spin crossover ($Fe^{II}_{LS} \rightarrow Fe^{II}_{HS}$) which occurs above 100 K.

Magnetic/photomagnetic measurements of $[Fe_3Co_2]$ were performed to test the possibility of recovering the high-spin Fe^{II} centers at low temperature using light irradiation as suggested by the reflectivity measurements (vide supra). These measurements involved cooling the sample in the absence of light (Figure 4, filled circles), followed by irradiation of the sample with white light for several hours at 5 K (Figure 4 inset), and then reheating of the sample with a sweep rate of 0.5 K/min without further

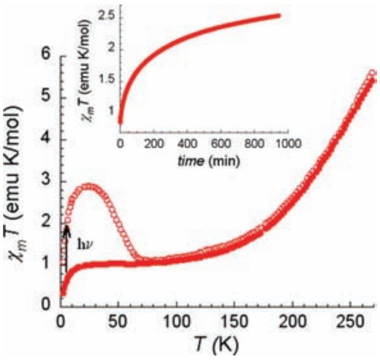


Figure 4. Temperature dependence of χ_mT of [Fe_3Co_2] at 1 T with a sweep rate of 0.5 K/min, before (filled circles) and after irradiation (open circles) with white light. Inset: time dependence of χ_mT under white light irradiation (3 mW/cm^2) at 5 K.

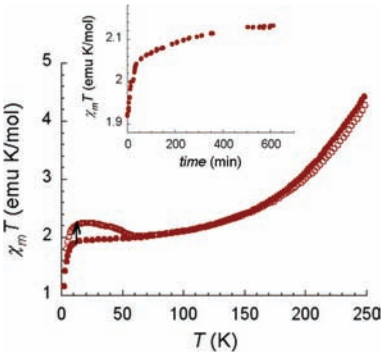


Figure 5. Temperature dependence of χ_mT of [Fe_3Fe_2] at 0.5 T at a sweep rate of 0.5 K/min, before (filled circles) and after irradiation (open circles) with white light (3 mW/cm^2). Inset: time dependence of χ_mT at 5 K of [Fe_3Fe_2] upon irradiation with white light (3 mW/cm^2).

irradiation (Figure 4, open circles). As already noted in previous studies on this compound,[65] between 140 and 300 K, the measurements in the dark reveal an incomplete spin crossover of the Fe^{II} ion from LS ($S = 0$) to HS ($S = 2$) in agreement with the Mössbauer spectroscopy results. Below 140 K, the residual paramagnetism observed in the χ_mT product highlights the presence of some $Fe^{II}{}_{HS}$ sites, also already reported in the previous measurements. Despite variations in humidity and solvent content in the microcrystals, the magnetic measurements were found to be consistent between samples of [Fe_3Co_2]. The time dependence of the χ_mT product at 5 K (Figure 4 inset) under white light irradiation (3 mW/cm^2) revealed photo-induced changes given that the χ_mT product increases from 0.8 emu·K/mol to 2.5 emu·K/mol after 16 h. Upon heating after irradiation, the χ_mT product increases from 1.09 emu·K/mol at 2 K up to 2.9 emu·K/mol at 25 K. This thermal behavior is likely the signature of the magnetic anisotropy of the HS Fe^{II} metal ions as observed in related Fe^{II} spin crossover systems[10] but could also be related to weak antiferromagnetic interactions between HS Fe^{II} sites through diamagnetic Co^{III} centers within the pentanuclear complex. By increasing the temperature at a sweep rate of ~0.5 K/min, complete relaxation of the photo-induced metastable HS Fe^{II} centers is observed at ~69 K, with an abrupt decrease in the χ_mT product from 35 K. Thus, above ~70 K, the two measurements before and after irradiation are nearly identical. When specific energies of light (488 nm, 530 nm, and 647 nm) were used to irradiate the compound, they were all found to excite the sample, with the red light being the most efficient (Supporting Information, Figure S3). Although the reflectivity measurements indicated that the photoexcitation is nearly quantitative at the surface of the material, the susceptibility measurements suggested a much less efficient conversion in the bulk, with a maximum photomagnetic susceptibility increase of 1.8 emu·K/mol (Figure 4), corresponding to only 20% of Fe^{II} centers converted from LS to HS with the irradiation.[73] This low photomagnetic conversion is likely a combination of several factors. First, the dark red color of the sample can significantly hinder light penetration, allowing for the excitation of only a small portion of the sample close to the irradiated surface. Second, previous studies on the [Fe_3Co_2] complex revealed that the three Fe^{II} centers do not show an equivalent spin crossover behavior.[65,67] Hence, the observed photo-induced spin crossover (with the light sources used) may involve only one or two of the three Fe^{II} centers. Finally, our measurements revealed that the photo-induced high-spin Fe^{II} centers relax even at 5 K. Therefore, with a temperature sweeping rate of about 0.5 K/min, high-spin Fe^{II} centers can relax during this time and exponentially faster as the temperature increases up to 69 K.

Reflectivity and Photomagnetic Studies of [Fe_3Fe_2]. As in the case of the [Fe_3Co_2] TBP complex, the photoactivity of the [Fe_3Fe_2] compound was first tested using optical techniques. The room temperature diffuse reflectance contains two absorbance bands (Supporting Information, Figure S1), one in the near-infrared region (NIR) with a maximum above 1000 nm and the second one at ~500 nm. It should be mentioned that the [Fe_3Co_2] and [Fe_3Fe_2] compounds both exhibit two maxima in the same energy ranges, but the NIR band is much more intense for the [Fe_3Fe_2] complex because of charge transfer between the Fe^{II} and Fe^{III} ions. Next, the optical reflectivity measurements were performed at various temperatures with concomitant white light irradiation (0.05 mW/cm^2). At room temperature, the data reveal two intense bands: one at 520 nm, which is analogous to the 540 nm band observed for [Fe_3Co_2], and another at energies higher than 1000 nm (Supporting Information, Figure S4). Overall, no significant variation in the reflectivity spectra was observed with temperature changes or irradiation. The spectra did not show evidence for photo-induced behavior, but, at the same time, they did not indicate the thermal spin crossover behavior which is known to occur according to magnetic susceptibility measurements performed in the dark.[65] Since the compound is intensely colored and strongly absorbs over most of the visible-NIR spectral range, there is only a small energy window (650−780 nm) over which optical changes will likely be observed. This situation rendered the reflectivity measurements difficult to analyze and not as sensitive as they are known to be for a less highly colored compound. For this reason, the photomagnetic properties of [Fe_3Fe_2] were tested by the same methods described for [Fe_3Co_2]. As in the case of [Fe_3Co_2], the measurements in the dark were consistent between samples, and the photoexcited state was generated at 5 K when the sample was irradiated with white light (Figure 5). The time dependence of the χ_mT product at 5 K (Figure 5 inset) under white light irradiation (3 mW/cm^2) indicates an initial value of 1.92 emu·K/mol and saturates around 2.13 emu·K/mol after 10 h. Because of the similarity of the two compounds, photomagnetic results were expected to be analogous to those observed for [Fe_3Co_2], but the average response for [Fe_3Fe_2] was surprisingly

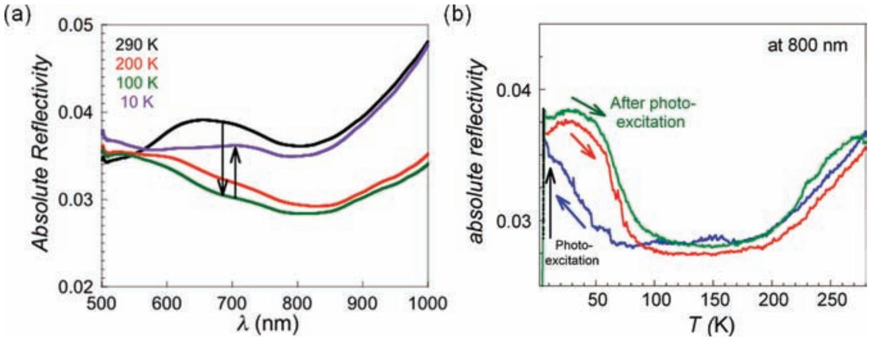


Figure 6. (a) Reflectivity spectra of [Co_3Fe_2] under continuous white light irradiation (0.05 mW/cm^2, dark, 290 K; red, 200 K; green, 100 K; purple, 10 K). (b) Absolute reflectivity at 800 nm (with 0.05 mW/cm^2 white light irradiation) with cooling (blue), heating (red), and heating after 40 min of white light irradiation at 5 K (0.05 mW/cm^2, green).

small, as confirmed by the thermal dependence of the $\chi_m T$ product (Figure 5). The maximum photomagnetic response observed, 0.15 emu·K/mol, corresponds to only 2% conversion of the Fe^{II} centers from LS to HS configurations. This result suggests that the photo-conversion occurs with a very weak efficiency even at the surface of the compound and thus does not propagate in the bulk of the sample.

The photomagnetic measurements were independently performed on different equipment, but the data consistently revealed a smaller photomagnetic response in [Fe_3Fe_2] than in [Fe_3Co_2]. Although factors such as sample quantity and irradiation conditions are generally plausible explanations for differences in photomagnetic properties, these issues are not the relevant ones in the present comparison. Indeed, these experimental parameters were intentionally kept as consistent as possible between the two compounds. Other factors, however, such as sample color (intensity of color), crystal size, and solvent content, are likely to be the reasons for the disparity in the results of these two analogous compounds. Crystal size and solvent content have already been shown to play important roles in the thermal spin crossover of TBP complexes.[63,65] One other possible explanation may be the darker color of the [Fe_3Fe_2] complex as compared to the [Fe_3Co_2] analogue which prevents efficient light penetration in the bulk solid in the former compound. A definitive analysis and conclusion of which parameters are dominant is not possible given the subtlety of the observed effects.

Reflectivity and Photomagnetic Studies of [Co_3Fe_2]. As with the other compounds, the photoactivity of the [Co_3Fe_2] complex was tested by optical techniques. The room temperature diffuse reflectance spectrum shows one broad absorption centered at ~800 nm (Supporting Information, Figure S5). This band falls within the expected range for metal—metal charge-transfer (MM′CT) bands and is therefore assigned to the excitation of Co^{III}—Fe^{II} pairs to Co^{II}—Fe^{III}; Co^{II} d-d transitions are also expected in this range, but the intensity of the observed band suggests that the MM′CT is dominant.[41] Optical reflectivity spectra at various temperatures under continuous white light irradiation (0.05 mW/cm^2) were collected. In agreement with the diffuse reflectance spectrum, the room temperature spectra revealed a very broad band centered at ~800 nm. As the temperature is lowered, the intensity of this 800 nm band varies significantly with temperature (Figures 6). The reflectivity in this region, illustrated by R_{800} (Figure 6b), decreases from 290 to 200 K and increases from 100 to 10 K. The decrease of R_{800} (i.e., an increase of absorbance) between 290 and 200 K is reminiscent of the gradual charge transfer between Co^{II} and Fe^{III} (Co^{II}/Fe^{III} → Co^{III}/Fe^{II}) that we had documented previously for this compound.[63] When the sample is further cooled to 10 K, an increase in R_{800} occurred that suggests a reverse charge-transfer from Fe^{II} to Co^{III} occurs (Co^{III}/Fe^{II} → Co^{II}/Fe^{III}). The similarity of the 290 and 10 K spectra indicates that there is a photo-induced charge transfer at low temperatures which yields the same product as at room temperature (Figure 6a); the similarity also suggests that, unlike the LIESST effect observed for [Fe_3Co_2], the charge transfer occurs quite efficiently with very weak irradiation (0.05 mW/cm^2) at the surface of the material. To confirm the photoexcitation process, spectra were measured for the sample at 5 K after being cooled in the absence of light and then irradiated during 40 min with white light (0.05 mW/cm^2, Supporting Information, Figure S6). As expected, the spectrum before irradiation at 5 K is very similar to the 200 and 100 K spectra, and there is a significant increase in the reflectivity around 800 nm after the irradiation. The temperature dependence of R_{800} suggests that a photo-induced charge transfer (Co^{III}/Fe^{II} → Co^{II}/Fe^{III}) is possible at low temperatures. Increasing the temperature at about 4 K/min, the photo-induced excited state thermally relaxes between 50 and 100 K (Co^{II}/Fe^{III} → Co^{III}/Fe^{II}), and the thermal-induced charge transfer (Co^{III}/Fe^{II} → Co^{II}/Fe^{III}) occurs above 200 K (Figure 6b).

The photomagnetic properties of [Co_3Fe_2] have been studied by magnetic susceptibility measurements with and without light irradiation. As we had noted previously,[63] measurements in the dark were found to vary somewhat between samples depending on the amount of interstitial water molecules. Not surprisingly, in the course of our studies, we discovered that the photomagnetic responses also varied between samples. To determine if the hydration level of the compound influenced the photomagnetic behavior, a series of measurements was performed on samples of the same batch of compound that had been exposed to humid air for different periods of time (Figure 7). In the first measurement, taken after only 5 min of exposure to humid air, the magnetic measurements in the dark were observed to be very different from any known measurement of the [Co_3Fe_2] blue solid. Instead, it was quite similar to measurements of the [Co_3Fe_2] phase referred to as the "red solid" (Figure 7, black line) which was subjected to detailed analysis in a prior piece of work.[63] The $\chi_m T$ value of the compound at room temperature is 10 emu K/mol in accord with three high spin Co^{II} ions (S = 3/2) and two low spin Fe^{III} ions (S = 1/2), both with strong orbital contributions.[63] This observation indicates that, in such a short period of time, the majority of the sample did not have the time

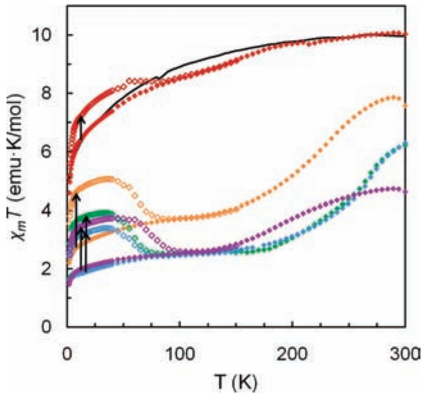


Figure 7. Temperature dependence of $\chi_m T$ of [Co_3Fe_2] (1.2−2.6 mg samples) at 0.1 T at a sweep rate of 1 K/min, before (filled) and after (open) irradiation with white light (40 mW/cm^2 for 4 h) as a function of time exposed to humid air: 5 min (red), 2 days (yellow), 5 days (green), 12 days (blue), and 22 days (purple). The black line represents the temperature dependence of $\chi_m T$ of [Co_3Fe_2] red solid.

Table 1. Water Content of Samples of [Co_3Fe_2] as Measured by TGA, after Being Exposed to Humid Air, and the Change in Magnetic Susceptibility Observed for Each Sample after White Light Irradiation

time in humid air	waters of hydration ($\pm$0.1 H_2O)	$\Delta\chi_m T$ at 30K
5 min	15.3 H_2O	0.77 emu K/mol
2 days	16.8 H_2O	1.90 emu K/mol
5 days	19.7 H_2O	1.77 emu K/mol
12 days	19.7 H_2O	1.32 emu K/mol
22 days	16.4 H_2O	1.51 emu K/mol

and/or sufficient water exposure to convert from the [$Co^{II}{}_3Fe^{III}{}_2$] state. However, a partial conversion to a less paramagnetic state of the compound ([$Co^{III}{}_2Co^{II}Fe^{II}{}_2$] or [$Co^{III}Co^{II}{}_2Fe^{II}Fe^{III}$]) is observed with decreasing temperature,[74] associated with a small photomagnetic response in the 2−50 K temperature range. TGA analysis of this sample revealed that it contains significantly fewer interstitial water molecules (about 15.3) than the expected 24 molecules, which was observed previously in a stable sample.[75] Samples from the same batch after 2, 5, 12, and 22 days of exposure to humidity were also studied (water contents listed in Table 1). Magnetic measurements in the dark are all found to be intermediate between the first measurement and the expected results for a stable sample.[63] Overall, there did not seem to be a relationship between the photomagnetic response and the water content (or the time exposed to humid air). The data did show, however, that as long as Co^{III}−Fe^{II} pairs are present in a sample at low temperature, a photomagnetic response is observed.

After these preliminary results were obtained, a stable compound which contains 23−24 water molecules was studied. The sample was measured after exposure of the original solid to humid air for six weeks. Magnetic susceptibility measurements were first obtained by cooling the sample in the dark to confirm that its thermal behavior (Figure 8) is in agreement with previous data and the presence of a [$Co^{III}{}_2Co^{II}Fe^{II}{}_2$] configuration.[63] Then the compound was irradiated at 10 K with a white light (~5 mW/cm^2) for approximately 1 h (Figure 8 inset). The magnetic susceptibility response increases quickly initially and begins to saturate only after 40 min as shown in the Figure 8 inset. The photoexcited state is "stable" up to ~50 K (with temperature sweeping rate of about 0.5 K/min), after which temperature the susceptibility decreases until it is equivalent to the dark measurement at 75 K.

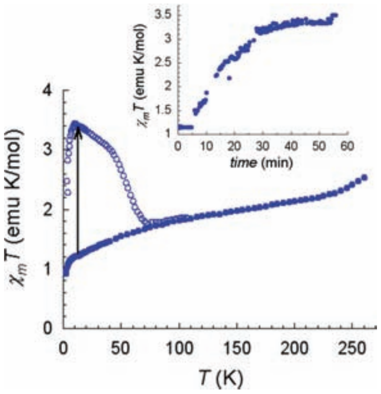


Figure 8. Temperature dependence of $\chi_m T$ of [Co_3Fe_2] at 0.1 T at a sweep rate of 0.5 K/min, before and after irradiation at 10 K with white light (3 mW/cm^2). Inset: Time dependence of $\chi_m T$ at 10 K of [Co_3Fe_2] upon irradiation with white light (3 mW/cm^2).

Considering the $\chi_m T$ product increase of about 2.9 emu K/mol at 10 K, it can be estimated that approximately 36% of the diamagnetic Co^{III}/Fe^{II} pairs have been excited in paramagnetic Co^{II}/Fe^{III} pairs, or about a third of the compound is converted from the [$Co^{III}{}_2Co^{II}Fe^{II}{}_2$] state to the [$Co^{II}{}_2Fe^{III}{}_2$] configuration.[76] The photo-conversion of the [$Co^{III}{}_2Co^{II}Fe^{II}{}_2$] state is thus incomplete. This low efficiency of the photoexcitation, as well as the slow saturation of the $\chi_m T$ product with time under irradiation (Figure 8 inset), is likely due to the very dark blue color of the sample which hinders light penetration and thus a bulk conversion of the material. Another possible explanation is that the $Co^{II}{}_3Fe^{III}{}_2$ redox state is not easily accessible in the blue solid form of the compound; previous studies on the [Co_3Fe_2] complex revealed only a partial CTISC at room temperature.[63] Measurements were also performed at various wavelengths (365−950 nm). Indeed, all energies of photons (Supporting Information, Figure S7) are able to photoinduce paramagnetic Co^{II}/Fe^{III} units. Among all the wavelengths tested, 950 nm near-infrared light was found to be the most efficient to photogenerate Co^{II}/Fe^{III} pairs, but no wavelength was found to relax these paramagnetic units at 30 K. Finally, white light was found to be the most efficient source overall.

■ CONCLUSIONS

In summary, three cyanide-bridged compounds from our previously reported family of trigonal bipyramidal (TBP) complexes have been studied vis-à-vis their photo-induced optical and magnetic properties. In all three cases, the compounds are photosensitive, and the photoexcited state has been found to correlate to the high temperature state of the molecules. In the case of the [Fe_3Co_2] analogue, the study of which was inspired by the [Fe(diimine)$_2$(NCS)$_2$] spin crossover family of compounds, exhibits a light-induced spin crossover (LIESST effect) at the equatorial Fe^{II} sites. The [Fe_3Fe_2] compound exhibits a similar effect as noted for [Fe_3Co_2], but the photo-conversion is far less pronounced. The [Co_3Fe_2] complex, a molecular analogue of the

Co/Fe Prussian blue family, undergoes a photo-induced charge transfer, which converts Co^{III}_{LS} and Fe^{II}_{LS} sites to Co^{II}_{HS} and Fe^{III}_{LS} sites. In the cases of $[Fe_3Co_2]$ and $[Co_3Fe_2]$, optical reflectivity measurements accurately predicted the photomagnetic behavior, which was confirmed by magnetic susceptibility data. In these cases, the low efficiency of the irradiation is attributed to the dark color of the samples.

Efforts are currently underway to increase the nuclearity and dimensionality of the spin crossover compounds to improve the cooperativity of the phenomenon. This is a feasible goal given the availability of six terminal cyanide ligands on the molecules and the fact that they are soluble and stable in solution. Indeed, studies from our laboratories in this vein have demonstrated that one can obtain large heterotrimetallic molecules with 11 metal centers[77] and extended structures[67] by using the trigonal bipyramidal molecules as building blocks. Additional investigations along these lines are clearly warranted.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Room temperature diffuse reflectance spectra, additional magnetic and photomagnetic measurements, and additional reflectivity spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: dunbar@mail.chem.tamu.edu (K.R.D.), clerac@crpp-bordeaux.cnrs.fr (R.C.), mathon@icmcb-bordeaux.cnrs.fr (C.M.).

■ ACKNOWLEDGMENT

We thank Prof. Curtis Berlinguette (University of Calgary) and Prof. Michael Shatruk (Florida State University) for their pioneering work on these compounds in the K.R.D. laboratories. We are grateful to Prof. Catalina Achim and Dr. Alina Dragulescu-Andrasi (Carnegie Mellon University) for their earlier collaborative work on the spin-crossover behavior of the compounds discussed herein. K.R.D. acknowledges the Department of Energy (Grant DE-FG03-02ER45999) for the support of this research which has provided all of the funds to prepare and characterize the compounds as well as to make X-ray and magnetic measurements at Texas A&M University. The Welch Foundation (A-1449) (a private foundation in the State of Texas) is acknowledged for summer support for K.E.F. during the course of her Ph.D. studies. We thank NSF for an equipment grant to purchase the SQUID magnetometer (NSF-9974899). C.M./R.C acknowledge the University of Bordeaux, the CNRS, Région Aquitaine, ANR (NT09_469563, AC-MAGnets project) and GIS Advanced Materials in Aquitaine (COMET Project) for research support. Marguerite Kalisz, Lionel Buisson, and Etienne Harté are also acknowledged for their expertise and assistance.

■ REFERENCES

(1) Entley, W. R.; Girolami, G. S. *Science* **1995**, *268*, 397–400.

(2) Ferlay, S.; Mallah, T.; Ouahès, R.; Veillet, P.; Verdaguer, M. *Nature* **1995**, *378*, 701–703.

(3) Holmes, S. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1999**, *121*, 5593–5594.

(4) Chapman, K. W.; Southon, P. D.; Weeks, C. L.; Kepert, C. J. *Chem. Commun.* **2005**, 3322–3324.

(5) Kaye, S. S.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 6506–6507.

(6) Boxhoorn, G.; Moolhuysen, J.; Coolegem, J. G. F.; Van Santen, R. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1305–1307.

(7) See, for example, http://www.fda.gov/Drugs/EmergencyPreparedness/BioterrorismandDrugPreparedness/ucm130334.htm.

(8) Dunbar, K. R.; Heintz, R. A. *Prog. Inorg. Chem.* **1997**, *45*, 283–391.

(9) Shatruk, M.; Avendaño, C.; Dunbar, K. R. *Prog. Inorg. Chem.* **2009**, *56*, 155–334.

(10) Létard, J.-F. *J. Mater. Chem.* **2006**, *16*, 2550–2559.

(11) Bleuzen, A.; Marvaud, V.; Mathonière, C.; Sieklucka, B.; Verdaguer, M. *Inorg. Chem.* **2009**, *48*, 3453–3466.

(12) McGarvey, J. J.; Lawthers, I. *J. Chem. Soc., Chem. Commun.* **1982**, 906–907.

(13) Decurtins, S.; Gütlich, P.; Köhler, C. P.; Spiering, H.; Hauser, A. *Chem. Phys. Lett.* **1984**, *105*, 1–4.

(14) Decurtins, S.; Gütlich, P.; Köhler, C. P.; Spiering, H. *J. Chem. Soc., Chem. Commun.* **1985**, 430–432.

(15) Herber, R.; Casson, L. M. *Inorg. Chem.* **1986**, *25*, 847–852.

(16) Baldenius, K. U.; Campen, A. K.; Hoehnk, H. D. *J. Mol. Struct.* **1987**, *157*, 295–299.

(17) Herber, R. H. *Inorg. Chem.* **1987**, *26*, 173–178.

(18) Figg, D. C.; Herber, R. H.; Potenza, J. A. *Inorg. Chem.* **1992**, *31*, 2111–2117.

(19) Lètard, J. F.; Nguyen, O.; Soyer, H.; Mingotaud, C.; Delhaès, P.; Kahn, O. *Inorg. Chem.* **1999**, *38*, 3020–3021.

(20) MacLean, E. J.; McGrath, C. M.; O'Connor, C. J.; Sangregorio, C.; Seddon, J. M. W.; Sinn, E.; Sowrey, F. E.; Teat, S. J.; Terry, A. E.; Vaughan, G. B. M.; Young, N. A. *Chem.—Eur. J.* **2003**, *9*, 5314–5322.

(21) Marchivie, M.; Guionneau, P.; Lètard, J. F.; Chasseau, D. *Acta Crystallogr., Sect. B: Struct. Sci.* **2005**, *B61*, 25–28.

(22) Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *272*, 704–705.

(23) Bleuzen, A.; Escax, V.; Ferrier, A.; Villain, F.; Verdaguer, M.; Münsch, P.; Itié, J.-P. *Angew. Chem., Int. Ed.* **2004**, *43*, 3728–3731.

(24) Bleuzen, A.; Lomenech, C.; Escax, V.; Villain, F.; Varret, F.; Cartier dit Moulin, C.; Verdaguer, M. *J. Am. Chem. Soc.* **2000**, *122*, 6648–6652.

(25) Cartier dit Moulin, C.; Champion, G.; Cafun, J.-D.; Arrio, M.-A.; Bleuzen, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 1287–1289.

(26) Cartier dit Moulin, C.; Villain, F.; Bleuzen, A.; Arrio, M.-A.; Sainctavit, P.; Lomenech, C.; Escax, V.; Baudelet, F.; Dartyge, E.; Gallet, J.-J.; Verdaguer, M. *J. Am. Chem. Soc.* **2000**, *122*, 6653–6658.

(27) Champion, G.; Escax, V.; Cartier dit Moulin, C.; Bleuzen, A.; Villain, F.; Baudelet, F.; Dartyge, E.; Verdaguer, M. *J. Am. Chem. Soc.* **2001**, *123*, 12544–12546.

(28) Escax, V.; Bleuzen, A.; Cartier dit Moulin, C.; Villain, F.; Goujon, A.; Varret, F.; Verdaguer, M. *J. Am. Chem. Soc.* **2001**, *123*, 12536–12543.

(29) Escax, V.; Champion, G.; Arrio, M.-A.; Zacchigna, M.; Cartier dit Moulin, C.; Bleuzen, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 4798–4801.

(30) Gawali-Salunke, S.; Varret, F.; Maurin, I.; Enachescu, C.; Malarova, M.; Boukheddaden, K.; Codjovi, E.; Tokoro, H.; Ohkoshi, S.; Hashimoto, K. *J. Phys. Chem. B* **2005**, *109*, 8251–8256.

(31) Sato, O.; Einaga, Y.; Fujishima, A.; Hashimoto, K. *Inorg. Chem.* **1999**, *38*, 4405–4412.

(32) Sato, Y.; Ohkoshi, S.-i.; Hashimoto, K. *J. Appl. Phys.* **2002**, *92*, 4834–4836.

(33) Shimamoto, N.; Ohkoshi, S.; Sato, O.; Hashimoto, K. *Inorg. Chem.* **2002**, *41*, 678–684.

(34) Rombaut, G.; Verelst, M.; Golhen, S.; Ouahab, L.; Mathonière, C.; Kahn, O. *Inorg. Chem.* **2001**, *40*, 1151–1159.

(35) Herrera, J. M.; Marvaud, V.; Verdaguer, M.; Marrot, J.; Kalisz, M.; Mathonière, C. *Angew. Chem., Int. Ed.* **2004**, *43*, 5468–5471.

(36) Mathonière, C.; Podgajny, R.; Guionneau, P.; Labrugere, C.; Sieklucka, B. *Chem. Mater.* **2005**, *17*, 442–449.

(37) Raghunathan, R.; Ramasesha, S.; Mathonière, C.; Marvaud, V. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2006**, *73*, 045131/1–045131/7.

(38) Ramasesha, S.; Raghunathan, R.; Ducasse, L.; Sutter, J. P.; Mathonière, C. *Phase Transitions* **2006**, *79*, 637–654.

(39) Mathonière, C.; Kobayashi, H.; Le Bris, R.; Kaiba, A.; Bord, I. *C. R. Chim.* **2008**, *11*, 665–672.

(40) Raghunathan, R.; Ramasesha, S.; Mathonière, C.; Marvaud, V. *Phys. Chem. Chem. Phys.* **2008**, *10*, 5469–5474.

(41) Li, D.; Clérac, R.; Roubeau, O.; Harté, E.; Mathonière, C.; Le Bris, R.; Holmes, S. M. *J. Am. Chem. Soc.* **2008**, *130*, 252–258.

(42) Zhang, Y.; Li, D.; Clérac, R.; Kalisz, M.; Mathonière, C.; Holmes, S. M. *Angew. Chem., Int. Ed.* **2010**, *49*, 3752–3756.

(43) Mercurol, J.; Li, Y.; Pardo, E.; Risset, O.; Seuleiman, M.; Rousselière, H.; Lescouëzec, R.; Julve, M. *Chem. Commun.* **2010**, *46*, 8995–8997.

(44) Létard, J.-F.; Real, J. A.; Moliner, N.; Gaspar, A. B.; Capes, L.; Cador, O.; Kahn, O. *J. Am. Chem. Soc.* **1999**, *121*, 10630–10631.

(45) Chastanet, G.; Letard, J.-F.; Gaspar, A. B.; Real, J. A. *Chem. Commun.* **2001**, 819–820.

(46) Gaspar, A. B.; Ksenofontov, V.; Spiering, H.; Reiman, S.; Real, J. A.; Gütlich, P. *Hyperfine Interact.* **2003**, *144/145*, 297–306.

(47) Chastanet, G.; Carbonera, C.; Mingotaud, C.; Létard, J.-F. *J. Mater. Chem.* **2004**, *14*, 3516–3523.

(48) Gaspar, A. B.; Ksenofontov, V.; Reiman, S.; Gütlich, P.; Thompson, A. L.; Goeta, A. E.; Munoz, M. C.; Real, J. A. *Chem.—Eur. J.* **2006**, *12*, 9289–9298.

(49) Moussa, N. O.; Trzop, E.; Mouri, S.; Zein, S.; Molnar, G.; Gaspar, A. B.; Collet, E.; Buron-Le Cointe, M.; Real, J. A.; Borshch, S.; Tanaka, K.; Cailleau, H.; Bousseksou, A. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *75*, 054101/1–054101/8.

(50) Fedaoui, D.; Bouhadja, Y.; Kaiba, A.; Guionneau, P.; Létard, J.-F.; Rosa, P. *Eur. J. Inorg. Chem.* **2008**, 1022–1026.

(51) Létard, J.-F.; Carbonera, C.; Real, J. A.; Kawata, S.; Kaizaki, S. *Chem.—Eur. J.* **2009**, *15*, 4146–4155.

(52) Pelleteret, D.; Clérac, R.; Mathonière, C.; Hartè, E.; Schmitt, W.; Kruger, P. E. *Chem. Commun.* **2009**, 221–223.

(53) Amoore, J. J. M.; Neville, S. M.; Moubaraki, B.; Iremonger, S. S.; Murray, K. S.; Létard, J.-F.; Kepert, C. J. *Chem.—Eur. J.* **2010**, *16*, 1973–1982.

(54) Kaiba, A.; Shepherd, H. J.; Fedaoui, D.; Rosa, P.; Goeta, A. E.; Rebbani, N.; Létard, J. F.; Guionneau, P. *Dalton Trans.* **2010**, *39*, 2910–2918.

(55) Breuning, E.; Ruben, M.; Lehn, J.-M.; Renz, F.; Garcia, Y.; Ksenofontov, V.; Gütlich, P.; Wegelius, E.; Rissanen, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 2504–2507.

(56) Nishihara, T.; Nihei, M.; Oshio, H.; Tanaka, K. *J. Phys.: Conf. Ser.* **2009**, *148*, 012033/1–012033/4.

(57) Wu, D.-Y.; Sato, O.; Einaga, Y.; Duan, C.-Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 1475–1478.

(58) Duriska, M. B.; Neville, S. M.; Moubaraki, B.; Cashion, J. D.; Halder, G. J.; Chapman, K. W.; Balde, C.; Létard, J.-F.; Murray, K. S.; Kepert, C. J.; Batten, S. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 2549–2552.

(59) Van Langenberg, K.; Batten, S. R.; Berry, K. J.; Hockless, D. C. R.; Moubaraki, B.; Murray, K. S. *Inorg. Chem.* **1997**, *36*, 5006–5015.

(60) Berlinguette, C. P.; Galán-Mascarós, J. R.; Dunbar, K. R. *Inorg. Chem.* **2003**, *42*, 3416–3422.

(61) Berlinguette, C. P.; Vaughn, D.; Cañada-Vilalta, C.; Galán-Mascarós, J. R.; Dunbar, K. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 1523–1526.

(62) Berlinguette, C. P.; Dragulescu-Andrasi, A.; Sieber, A.; Galán-Mascarós, J. R.; Güdel, H.-U.; Achim, C.; Dunbar, K. R. *J. Am. Chem. Soc.* **2004**, *126*, 6222–6223.

(63) Berlinguette, C. P.; Dragulescu-Andrasi, A.; Sieber, A.; Güdel, H.-U.; Achim, C.; Dunbar, K. R. *J. Am. Chem. Soc.* **2005**, *127*, 6766–6779.

(64) Shatruk, M.; Chambers, K. E.; Prosvirin, A. V.; Dunbar, K. R. *Inorg. Chem.* **2007**, *46*, 5155–5165.

(65) Shatruk, M.; Dragulescu-Andrasi, A.; Chambers, K. E.; Stoian, S. A.; Bominaar, E. L.; Achim, C.; Dunbar, K. R. *J. Am. Chem. Soc.* **2007**, *129*, 6104–6116.

(66) Hilfiger, M. G.; Shatruk, M.; Prosvirin, A.; Dunbar, K. R. *Chem. Commun.* **2008**, 5752–5754.

(67) Funck, K. E.; Hilfiger, M. G.; Berlinguette, C. P.; Shatruk, M.; Wernsdorfer, W.; Dunbar, K. R. *Inorg. Chem.* **2009**, *48*, 3438–3452.

(68) Hilfiger, M. G.; Chen, M.; Brinzari, T. V.; Nocera, T. M.; Shatruk, M.; Petasis, D. T.; Musfeldt, J. L.; Achim, C.; Dunbar, K. R. *Angew. Chem., Int. Ed.* **2010**, *49*, 1410–1413.

(69) Wang, X.-Y.; Hilfiger, M. G.; Prosvirin, A.; Dunbar, K. R. *Chem. Commun.* **2010**, *46*, 4484–4486.

(70) The humidity of the laboratories at Texas A&M University averaged 62−76% in the winter months of 2008−2009 during which this study was conducted.

(71) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, Germany, 1989.

(72) König, E.; Madeja, K. *Inorg. Chem.* **1967**, *6*, 48–57.

(73) As reported in reference 65, 66% of the $\mathrm{Fe}^{\mathrm{II}}$ centers are in the HS state at room temperature.

(74) This idea was originally hypothesized in ref 63 as one contribution to the decrease in $\chi_{\mathrm{m}}T$ below 50 K.

(75) Although it was originally prepared in acetonitrile, previous work (ref 63) suggests that the complex crystallizes only with interstitial water molecules; hence, the interstitial solvent in the 5 min sample is assumed to be solely water.

(76) The increase could also correspond to 72% of the complexes converting from $\mathrm{Co}^{\mathrm{III}}{}_2\mathrm{Co}^{\mathrm{II}}\mathrm{Fe}^{\mathrm{II}}{}_2$ to $\mathrm{Co}^{\mathrm{III}}\mathrm{Co}^{\mathrm{II}}{}_2\mathrm{Fe}^{\mathrm{II}}\mathrm{Fe}^{\mathrm{III}}$.

(77) Berlinguette, C. P.; Dunbar, K. R. *Chem. Commun.* **2005**, 2451–2453.