Inorg. Chem. **2004**, *43*, 6875–6877

Inorganic Chemistry
Communication

Observation of Hysteretic Bistability in $[Co^{III}Cp_2]^+[Fe^{III}I_4]^-$

Jesse M. Migliori,[†] William M. Reiff,*[,‡] Atta M. Arif,[†] and Joel S. Miller*[,†]

Department of Chemistry, University of Utah, 315 S. 1400 E. Street, Room 2124,
Salt Lake City, Utah 84112-0850, and Department of Chemistry and Chemical Biology,
Northeastern University, Boston, Massachusetts 02115

Received July 24, 2004

$[Co^{III}Cp_2]^+[Fe^{III}I_4]^-$ (Cp = cyclopentadienyl) prepared by the double oxidation of FeI_2 and $CoCp_2$ with iodine exhibits a 30 °C thermal hysteresis in magnetic susceptibility between 134 and 164 K that is attributed to a phase transition to a disordered triclinic unit cell from an ordered monoclinic unit cell upon cooling.

Bistable materials, i.e., materials that can persist in two relatively stable states, each with different physical properties (optical, electrical, magnetic, and/or mechanical properties), have great potential in next-generation sensor, switching, and/or actuator devices and even in so-called "smart" systems.[1] Bistable materials are rare and range from molecules, such as spin-crossover materials,[2,3] to liquid crystals,[4] to solid state 2- and 3-D network structured materials, such as piezoelectric and magnetic materials. Especially important are materials exhibiting hysteresis that enables two states to be stable, for example, at the same temperature. Hysteresis is especially rare for molecule-based materials, but it is sought for many applications. Thermal hysteresis is observed for several spin-crossover materials and more recently in the magnetic behavior of 1,3,5-trithia-2,4,6-triazapentalenyl[5] and spiro-biphenalenyl radicals.[6] Herein, we report thermal hysteresis of the magnetic susceptibility of the molecule-based solid $[Co^{III}Cp_2]^+[Fe^{III}I_4]^-$ (Cp = cyclopentadienyl).

$[Co^{III}Cp_2][Fe^{III}I_4]$**,** prepared from $CoCp_2$, FeI_2, and I_2 under an inert atmosphere,[7] exhibits a monoclinic unit cell at 150 K with a solid-state structure[8] consisting of segregated chains of cations and anions along the *a* axis and alternating ionic layers (in the *ac* plane) that are stacked along the *b* axis (Figure 1). Adjacent parallel chains of cations are canted with respect to each other, and adjacent parallel chains of anions have their tetrahedra pointing in opposite directions. The Fe−I distance ranges from 2.537 to 2.551 Å and averages 2.543 Å. The I···I separations within $[Fe^{III}I_4]^-$ range from 4.099 to 4.182 Å and average 4.143 Å. This is comparable to the shortest intermolecular $[FeI_4]^-$ I···I separations that range from 4.057 to 4.382 Å and average 4.182 Å. In addition to the short I···I separation along *a*, comparable short I···I separations of 4.190 and 4.297 Å are present that alternate along *c*. These I···I separations are in accord with van der Waals interactions[9] and provide close contacts for (antiferromagnetic) exchange interactions among the $[Fe^{III}I_4]^-$ anions that form layers in the *ab* plane.

The temperature dependence of the magnetic susceptibility, χ, for a polycrystalline sample is plotted as $\chi T(T)$ for both decreasing ($T_\downarrow$) and increasing ($T_\uparrow$) temperature (Figure 2). High-spin, $S = {}^5/_2$, Fe^{III} is the only paramagnetic ion present in $[Co^{III}Cp_2]^+[Fe^{III}I_4]^-$. The observed room-temperature χT value of 4.64 emu·K/mol slightly exceeds the expected spin-only value of 4.375 emu·K/mol and is slightly greater than 4.50 emu·K/mol reported for $[NEt_4][FeX_4]$ (X = Cl, Br).[10] Because of antiferromagnetic exchange between the $S = {}^5/_2$ Fe^{III} sites, as the temperature is decreased, $\chi T(T)$ decreases

---

* To whom correspondence should be addressed. E-mail: jsmiller@chem.utah.edu (J.S.M.).

[†] University of Utah.

[‡] Northeastern University.

(1) Kahn, O. *Chemtronics* **1988**, *3*, 140.

(2) See, e.g.: Gütlich, P.; Hauser, A.; Spiering, H. *Angew. Chem., Int. Ed.* **1994**, *33*, 2024.

(3) Kahn, O.; Martinez, C. J. *Science* **1998**, *279*, 44; Kahn, O.; Kröber, J.; Jay, C. *Adv. Mater.* **1992**, *4*, 718.

(4) e.g., Eidenschink, R. *Adv. Mater.* **1989**, *1*, 1424. Escher, K. C.; Winger, R. *Adv. Mater.* **1992**, *4*, 189.

(5) Fujita, W.; Awaga, K. *Science* **1999**, *286*, 261. Fujita, W.; Awaga, K.; Matsuzki, H.; Okamoto, H. *Phys. Rev. B* **2002**, *65*, 64434. McManus, G. D.; Rawson, J. M.; Feeder, van Duijn, N.; McInnes, J. L.; Novoa; J. J. Burriel, R.; Palacio, F.; Oliet, P. *J. Mater. Chem.* **2001**, *11*, 1992.

(6) Itkis, M. E.; Chi, X.; Cordes, A. W.; Haddon, R. C. *Science* **2002**, *296*, 1443.

(7) I_2 (120 mg) dissolved in 150 mL of CH_2Cl_2 was added to a solution containing $CoCp_2$ (100 mg) and FeI_2 (162.5 mg) dissolved in 50 mL of CH_2Cl_2. After the mixture had been stirred overnight and filtered, the volume was decreased to 5 mL, and a black precipitate was collected by filtration and dried (yield 55%). %C calcd (obs), 15.96 (16.39); %H, 1.34 (1.22).

(8) Unit cell: centrosymmetric monoclinic $P2_1/m$ (No. 11) space group; $a = 7.2455$ (2) Å, $b = 16.2229$ (5) Å, $c = 14.5930$ (3) Å, $\beta = 94.2371$ (15)°, $Z = 4$, $T = 150$ K, $V = 1710.62$ (8) Å^3. The X-ray CIF file has been deposited with the Cambridge Crystallographic Data Center, ref no. CCDC-236539.

(9) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. Pauling, L. *Nature of the Chemical Bond*, 3rd ed; Cornel University Press: Ithaca, NY, 1960. Rowland, R. S.; Taylor, R. *J. Chem. Phys.* **1996**, *100*, 7384.

(10) Ginsberg, A. L.; Robin, M. B. *Inorg. Chem.* **1963**, *2*, 817.

10.1021/ic049000g CCC: $27.50

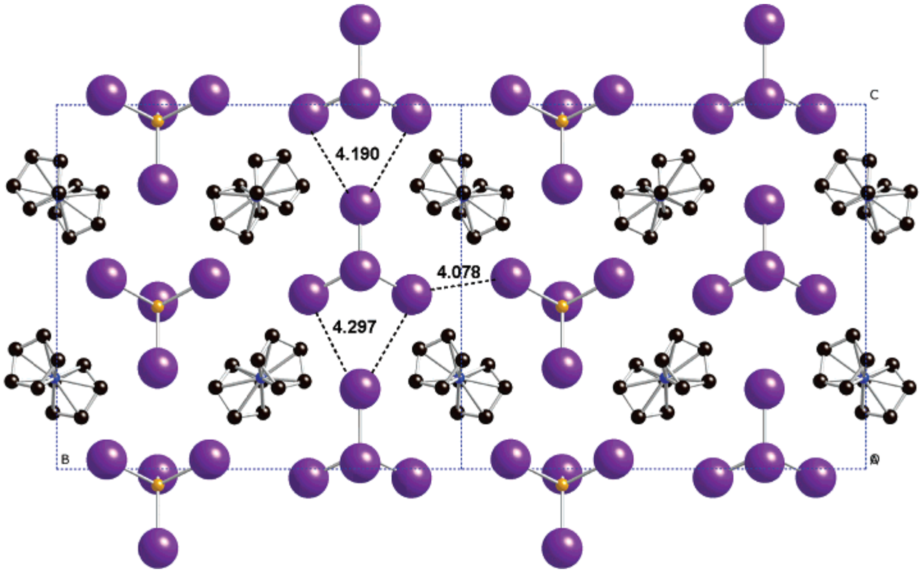

Figure 1. View of the structure of $[\mathrm{Co^{III}Cp_2}]^+[\mathrm{Fe^{III}I_4}]^-$ along the *a* axis.

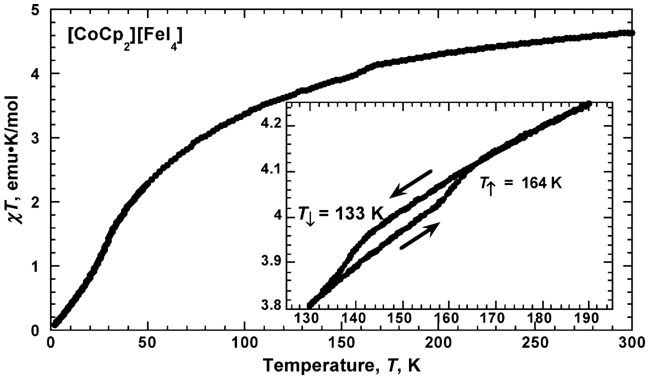

Figure 2. $\chi T(T)$ for $[\mathrm{Co^{III}Cp_2}]^+[\mathrm{Fe^{III}I_4}]^-$ in the region showing a ~30 °C thermal hysteresis with the $\chi T(T)$ divergence temperatures indicated in the figure.

to 3.96 emu•K/mol at ~148 K. However, at 143 K, $\chi T(T)$ begins to drop more rapidly until ~134 K, at which point the rate of decrease again is comparable to that observed above 143 K. The data above 143 K can be fit to the Curie–Weiss expression, $\chi \propto (T - \theta)^{-1}$, with $\theta = -56$ K. The relatively rapid drop in $\chi T(T)$ starting at 143 K suggests a phase transition. After the material had been cooled to 130 K, $\chi T(T)$ was measured as a function of increasing temperature, and a plot of $\mathrm{d}(\chi T)/\mathrm{d}T$ between 143 and 130 K is similar to that observed upon cooling between 143 and 159 K. Between 130 and 159 K, the data can be fit to the Curie–Weiss expression with $\theta = -79$ K.[11] Between 159 and 163 K, $\chi T(T)$ rises more rapidly; however, above 164 K, the original rate of change occurs.[12a] Hence, $\chi T(T)$ exhibits hysteresis with $T_\downarrow = 134$ K and $T_\uparrow = 164$ K, a thermal hysteresis, ΔT, of 30 ± 1 K, which is consistent with a first-order phase change. Preliminary differential scanning calorimetry (DSC) confirms first-order behavior ($\Delta H \approx -2.25$ kJ/mol) whose onset is ~163 K on cooling.

Table 1. Unit Cell Parameters for $[\mathrm{Co^{III}Cp_2}][\mathrm{Fe^{III}\ I_4}]$ as a Function of Temperature

T, K	150	125	150	200
unit cell	monoclinic	triclinic	triclinic	monoclinic
a, Å	7.255	9.549	9.581	7.249
b, Å	16.250	11.138	11.174	16.328
c, Å	14.612	16.201	16.296	14.664
α	90°	89.504°	89.252°	90°
β	94.223°	90.154°	89.967°	94.303°
γ	90°	90.340°	90.218°	90°
V, Å^3	1718.2	1723.0	1744.5	1730.6
mosaicity	0.404	1.954	1.923	1.712

The hysteresis was also followed by monitoring the unit cell parameters as a function of temperature (Table 1). At 150 K, $[\mathrm{CoCp_2}][\mathrm{FeI_4}]$ has a monoclinic unit cell with the structure as discussed above. Upon cooling to 125 K, a phase transition to a triclinic unit cell occurs with an increase in crystallographic mosaicity arising from small crystalline blocks tilted slightly with respect to each other,[13] indicative of disorder occurring upon cooling. The unit cell remains triclinic upon rewarming to 150 K, and the high residual mosaicity in the range of 125 and 150 K thwarted a refinement of the structure. On further warming to 200 K, the unit cell parameters slowly change to those of the original 150 K structure.

The phase transition is attributed primarily to either orientation changes or distortions of the anion, as the anions are paramagnetic and the observed behavior appears to be strongly associated with a change in $\chi T(T)$. Distinct $\mathrm{Fe^{III}}$ sites are not evident from the ^{57}Fe Mössbauer spectra of the rapidly relaxing paramagnetic phase of this material.[12] Phase transitions are reported for $[\mathrm{NEt_4}][\mathrm{Fe^{III}X_4}]$ (X = Cl, Br) at 22.6 and 236.1 K but are attributed to reorientation of the cation.[14] In contrast, DSC,[15a] heat capacity,[15b] and ESR[15c] investigations of the related $[\text{tetraalkylammonium}]_2[\mathrm{M^{II}Cl_4}]^{2-}$

---

(11) χ^2 to verify goodness of fit of the measured data with the expected Curie–Weiss expression from 130 to 159 K is 0.031.

(12) (a) The magnetic behavior at lower temperatures is complex and is being investigated further. (b) The material orders below 31 K and exhibits two ^{57}Fe hyperfine patterns suggesting averaging of magnetically nonequivalent $[\mathrm{FeI_4}]^-$ sites at higher temperature.

(13) Giacovazzo, C. *Fundamentals of Crystallography*; Oxford Science Publications: Oxford, U.K., 1992.

(M = Mn, Fe, Co, Ni, Cu, Zn) indicate both first-order and diffuse so-called λ structural phase transitions,[15d] which can be attributed to complex motions of *both the cation and anion* and *cooperativity* among these motions with decreasing temperature. Furthermore, the study of the single-crystal anisotropy of $[Et_4N]_2[NiCl_4]$ indicates a reversible, hysteretic discontinuity in $\Delta\chi$ centered at ~218 K with a smaller thermal hysteresis (~10 K) than observed herein.[16] Hence, the behavior observed herein cannot be attributed solely to motions of $[Fe^{III}I_4]^-$. This is especially the case as an X-ray investigation of $[Fe^{III}Cp_2]^+[Fe^{III}Cl_4]^-$ confirms a phase transition arising from Cp conformation changes within the cations.[17] However, high-resolution SQUID magnetization studies of polycrystalline $[FeCp_2][FeCl_4]$ (and $[FeCp_2][FeBr_4]$) do not reveal evidence of any structural phase transformations.[18] This is in contrast to $S = {}^1/_2$ decamethylmanganocene that undergoes a reversible structural phase transition with a small orientational change on cooling[19a] and exhibits a change in $\chi T(T)$ behavior at 253 K, but without hysteresis.[19b] Preliminary studies on $[Fe^{III}Cp_2][Fe^{III}I_4]$ reveal two reversible hysteretic transitions in $\chi T(T)$, suggesting that the facile observation in the magnetization studies is unique to $[Fe^{III}I_4]^-$. In the absence of low-temperature structure determinations, the temperature dependence of ESR spectra in the context of the line width changes for the $[Fe^{III}I_4]^-$ anion signal and far-IR spectra in the metal−halogen stretching region are needed to identify the genesis of the phase transition.

Acknowledgment. The authors gratefully acknowledges partial support from the ACS-PRF (PRF 36165-AC5), the U.S. Department of Energy (Grant DE-FG03-93ER45504), the National Science Foundation (Grant CHE 0110685), and the Air Force Office of Scientific Research (Grant F49620-00-1-0055. W.M.R. is grateful to the NSF-DMR for funds (Grant DMR-0114132) used for the purchase of a SQUID magnetometer. This work is dedicated to Philipp Gütlich on the occasion of his 70th birthday.

Supporting Information Available: Crystallographic data (atomic positions, thermal parameters, bond lengths, etc.) for $[Co^{III}Cp_2][Fe^{III}\ I_4]$ in the form of a CIF file. The materials is available free of charge via the Internet at http://pubs.ac.org.

IC049000G

---

[14] Navarro, R.; Puertolas, J. A.; Palacio, F.; Gonzales, D. *J. Chem. Therm.* **1988**, *20*, 373.

[15] (a) Melia, T. P.; Merrifield, R. *J. Chem. Soc. A* **1970**, 1166. (b) Melia, T. P.; Merrifield, R. *J. Chem. Soc. A* **1971**, 1258. (c) Bencini, A.; Benelli, C.; Gatteschi, D. *Inorg. Chem.* **1980**, *19*, 1632. (d) McCullough, P. *Pure Appl. Chem.* **1961**, *2*, 221.

[16] Gerloch, M.; Slade, R. C. *J. Chem. Soc. A*, **1969**, 1022.

[17] Cotton, F. A.; Daniels, L. M.; Pascual, I. *Acta Crystallogr.* **1998**, *C54*, 1575.

[18] Reiff, W. M.; Miller, J. S. Unpublished results.

[19] (a) Augart, N.; Boses, R.; Schmid, G. *Z. Anorg. Allg. Chem.* **1991**, *595*. 27. (b) McLean, R. S.; Miller, J. S. University of Utah, Salt Lake City, Utah. Unpublished results.