Inorg. Chem. **2008**, *47*, 7768−7774

Inorganic Chemistry
Article

Structure and Properties of $[Cr^{III}F(NCMe)_5](BF_4)_2 \cdot MeCN$: A Nonaqueous Source of $Cr^{III}F^{2+}$ and a Building Block for New Prussian-Blue-Like Magnetic Materials

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Received May 7, 2008

$[Cr^{III}F(NCMe)_5](BF_4)_2 \cdot MeCN$ (**1**) was synthesized from a prolonged dissolution of $[Cr^{III}(NCMe)_6](BF_4)_3$ in MeCN via fluoride abstraction from BF_4^-. Complex **1** exhibits a crystal field splitting, Δ_o, of 17 470 cm^{-1} and is a nonaqueous source of $Cr^{III}F^{2+}$. The reaction of **1** with $(NEt_4)_3[Cr^{III}(CN)_6]$ formed a new Prussian-blue-like magnetic material of $(NEt_4)_{0.04}[Cr^{III}F]_{1.54}[Cr^{III}(CN)_6](BF_4)_{0.12} \cdot 0.10(MeCN)$ (**2**) composition. Complex **2** magnetically orders at a critical temperature, T_c, of 85 K and at 2 K exhibits magnetic hysteresis with a coercive field, H_{cr}, of 60 Oe and a remanent magnetization, M_{rem}, of 1880 emuOe/mol.

Introduction

Over the past half century, various studies were performed on metal fluoride materials, leading to important information about their structure and bonding in molecular complexes,[1] in addition to extended ionic solids.[2] There have also been reports on their chemical reactivity and formation,[3] as well as in several applications of optical devices (i.e., optical fibers and scintillation counters).[4] Fluoride-containing materials have also showed promise in the development of molecule-based magnetic materials; for example, the formation of cyclic chromium-fluoride cage compounds has been reported,[5] where superparamagnetic-like properties (known as single-molecule magnets) are possible.[6] In addition to Cr−F cages, a novel spin frustrated triangular manganese fluoride cluster containing tetrazole ligands displaying two-dimensional (2D) antiferromagnetic ordering was recently reported.[7] Finally, several fluoride-bridging compounds with a Kagome structure where magnetic behaviors range from

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10.1021/ic800837f CCC: $40.75

weak short-range antiferromagnetic interactions to long-range magnetic ordering have been reported,[8] and in one case where fluoride bridges link Fe^{III} ions together, along with bridging oxygen's, a spin-crossover phenomenon is observed.[9]

Our group has sought to discover nonaqueous sources of trivalent metal ions to enable the discovery of new materials. While $[M^{II}(NCMe)_x]^{2+}$ (M = V, Cr, Mn, Fe, Co, Ni, Cu) are abundant and widely used,[10] it was not until recently that the first $[M^{III}(NCMe)_6]^{3+}$, namely, M = Cr, was reported.[11] $[Cr^{III}(NCMe)_6]^{3+}$ was characterized to be $\sim 10^4$ more labile than $[Cr^{III}(OH_2)_6]^{3+}$ and enabled the formation of $Cr^{III}[M^{III}(CN)_6]$ (M = V, Cr, Mn, Fe) Prussian-blue (PB)-like materials, with a magnetic ordering Néel temperature, T_N, as high as 126 K being observed for $Cr^{III}[Cr^{III}(CN)_6] \cdot 0.16(MeCN)$.[12]

Upon reinvestigating $[Cr^{III}(NCMe)_6](BF_4)_3$, a dark purple crystalline material was isolated and characterized to be $[Cr^{III}F(NCMe)_5](BF_4)_2 \cdot MeCN$ (**1**), whose aqueous analogue, $[Cr^{III}F(OH_2)_5]^{2+}$, was previously reported in the 1960s.[13] In addition, several kinetic studies on the rate of aquation,[14] the electronic structure,[15] and redox potentials have been performed.[16] Compound **1** is the first reported nonaqueous source of $Cr^{III}F^{2+}$, and given the number of applications of metal fluoride-containing materials, we sought to incorporate the $Cr^{III}F^{2+}$ structural motif into new magnetic materials based upon a PB-like material.[17] Numerous reports on dinuclear complexes containing this $Cr^{III}F^{2+}$ motif in addition to a μ-cyano bridging ligand have been reported;[18] however, to the best of our knowledge, no reports have been made incorporating this motif into a PB-like material. Herein, the synthesis and characterization of **1** as well as its reaction with $(NEt_4)_3[Cr^{III}(CN)_6]$ forming a new PB-like material is described.

Experimental Section

All manipulations were carried out under a dry N_2 atmosphere (<1 ppm O_2) using Schlenk techniques or in a Vacuum Atmospheres DriLab. $(NEt_4)_3[Cr(CN)_6]$[19] and $[Cr^{III}(NCMe)_6](BF_4)_3$[11] were prepared by previously reported synthetic routes. Acetonitrile (MeCN) was purified through an activated alumina dual-column purification system[20] under a positive pressure of N_2, while diethyl ether (Et_2O) was purified via distillation under positive dry N_2 pressure over sodium dispersion (Strem) and benzophenone (Lancaster).

$[Cr^{III}F(NCMe)_5](BF_4)_2 \cdot MeCN$, 1. Complex **1** was synthesized by the dissolution of light orange $[Cr^{III}(NCMe)_6](BF_4)_3$ (97.9 mg, 0.175 mmol) in 10 mL of MeCN with a Teflon-coated stirrer for 72 h. The solution turned dark violet and after vacuum filtration; it was concentrated to 5 mL and set up for vapor diffusion with Et_2O. After 36 h, violet prisms formed which were collected via vacuum filtration, washed with copious amount of Et_2O, and dried under a vacuum for 30 min at room temperature (yield: 48.7 mg, 56.5%). Some violet prisms were collected and stored under the presence of the mother liquor, and the structure of **1** was characterized by single-crystal X-ray diffraction. Thermogravimetric analysis showed that the sample began to lose sample mass at a relatively low temperature (~40 °C; Figure S1, Supporting Information). Selected IR data (KBr) follows. ν_{CH}: 3015 (m), 2947 (m). ν_{CN}: 2332 (s), 2305 (s), 2252 (w), 1419 (m), 1368 (m), 1288 (m). ν_{BF}: 1051 (vs), 955 (m), 874 (w), 843 (w), 765 (w). ν_{CrF}: 640 (s), 522 (m), 432 cm^{-1} (s).

$(NEt_4)_{0.04}[Cr^{III}F]_{1.54}[Cr^{III}(CN)_6](BF_4)_{0.12} \cdot 0.10(MeCN)$, 2. Complex **2** was synthesized by slowly adding 10 mL of a yellow MeCN solution of $(NEt_4)_3[Cr^{III}(CN)_6]$ (229.6 mg, 0.3833 mmol, 2 equiv)

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via a syringe pump at a rate of 2 mL/h into a stirring, violet 20 mL MeCN solution of $[Cr^{III}F(NCMe)_5](BF_4)_2 \cdot MeCN$ (282.3 mg, 0.5751 mmol, 3 equiv). This forms an immediate dark olive green precipitate. After complete addition of the $[Cr^{III}(CN)_6]^{3-}$ solution, the mixture was stirred for 12 h. The dark olive green product was collected via centrifugation, and the colorless supernate was decanted off. The product was washed with MeCN (3 × 15 mL), followed by 15 mL of Et_2O, and dried at room temperature under a vacuum for 12 h. A dark olive green solid was isolated in a quantitative yield. Anal. calcd[21] for $(NEt_4)_{0.04}[Cr^{III}F]_{1.54}[Cr^{III}(CN)_6](BF_4)_{0.12} \cdot 0.10(MeCN)$, $C_{6.52}H_{1.10}N_{6.14}B_{0.12}Cr_{2.54}F_{2.02}$: C, 23.23; H, 0.33; N, 25.51; Cr, 39.17. Found: C, 22.84; H, 0.76; N, 25.93; Cr, 39.56. Thermogravimetric analyses coupled with mass spectroscopy (TGA/MS) analysis showed the sample was thermally unstable at relatively low temperatures (50 °C), above which solvent loss and decomposition occur simultaneously (Figure S2, Supporting Information). Due to this thermal instability, all samples were stored at −25 °C, and handling of these samples at ambient temperatures was minimized. Key selected IR data (KBr) are as follows. ν_{NCMe}: 2323 (s), 2296 (s), 2252 (w). ν_{CN}: 2168 (s) [half-width at half-height (hwhh): 22 cm^{-1}]. ν_{BF}: 1068 (m) cm^{-1}.

Infrared spectra were recorded from 400 to 4000 cm^{-1} on a Bruker Tensor 37 IR (±1 cm^{-1}) as KBr pellets. Centrifugation of the samples was performed using a Clay Adams centrifuge with a fixed rotary speed of 3200 rpm. Samples were centrifuged for 10 min to separate the precipitate from the mother liquor. TGA/MS measurements were performed on a TA Instruments Model 2050 TGA analyzer coupled to a Thermolab TL1285 thermal analysis/mass spectrometer. The TGA operates between ambient temperature and 1000 °C and is located in a Vacuum Atmospheres DriLab under an inert N_2 atmosphere. TGA samples were handled in a dry nitrogen atmosphere and heated under a nitrogen purge. Heating rates were 5 and 10 °C/min. Elemental analyses were performed by GCL & Chemisar Laboratories (Guelph, Ontario, Canada) on freshly prepared samples that were sealed under a dry nitrogen atmosphere and sent off for analysis.

Powder X-ray diffraction (PXRD) scans were obtained on a $\theta\angle\theta$ Bruker AXS D8 advance diffractometer (2θ of 12.5 to 42.5°, step width of 0.02°, counting time of 10 s/step, voltage of 40 kV, and current of 40 mA) fitted with a Göbel mirror to remove all but the Cu Kα radiation ($\lambda = 1.54060$ Å). Samples were sealed under an inert atmosphere in 1.00-mm thin-walled quartz capillaries to prevent oxidation and moisture absorption, and scans were performed at room temperature (~298 K).

Magnetic susceptibility measurements were made between 2 and 300 K using a Quantum Design MPMS-5 5T SQUID magnetometer with a sensitivity of 10^{-8} emu or 10^{-12} emu/Oe at 1 T and equipped with the ultralow field (~5 mOe), reciprocating sample measurement system, and continuous low-temperature control with enhanced thermometry features, or using a Quantum Design PPMS-9 ac/dc susceptometer. Measurements were made on powders contained in airtight Delrin holders supplied by Quantum Design. Small amounts of quartz wool were used in the Delrin holders to minimize the movement of the powders during measurements. The data were corrected for the measured diamagnetism of each holder, and core diamagnetic corrections of −251 and -131×10^{-6} emu/mol were calculated from Pascal's constants for $[Cr^{III}F(NCMe)_5](BF_4)_2 \cdot MeCN$ (**1**) and $(NEt_4)_{0.04}[Cr^{III}F]_{1.54}[Cr^{III}(CN)_6](BF_4)_{0.12} \cdot 0.10(MeCN)$ (**2**), respectively.

Table 1. Summary of Crystallographic Data for $[Cr^{III}F(NCMe)_5](BF_4)_2 \cdot MeCN$, **1**

	$[Cr^{III}F(NCMe)_5](BF_4)_2 \cdot MeCN$, **1**
empirical formula	$C_{12}H_{18}B_2CrF_9N_6$
fw, g/mol	490.94
temp, K	100(2)
space group	$P2_1/n$
a, Å	14.3450(103)
b, Å	8.0300(5)
c, Å	18.9130(12)
α, deg	90
β, deg	94.9300(10)
γ, deg	90
Z	4
V, Å^3	2170.5(2)
density (calculated), Mg/m^3	1.502
abs coeff, μ, mm^{-1}	0.612
R1	0.0341
wR2	0.0396
wavelength, Å	0.71069

The single-crystal X-ray diffraction studies were carried out on a Bruker APEX CCD diffractometer equipped with Mo Kα radiation ($\lambda = 0.71069$). A 0.20 × 0.20 × 0.07 mm purple plate of **1** was mounted on a cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ω scans. The crystal-to-detector distance was 60 mm, and the exposure time was 20 s/frame using a scan width of 0.3°. Data collection was 99.9% complete to 25.00° in θ. A total of 18 133 reflections were collected covering the indices $-18 < h < 19$, $-10 < k < 10$, $-23 < l < 24$. 5070; reflections were found to be symmetry-independent, with an R_{int} of 0.0221. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2_1/n$. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SIR-97) produced a complete heavy-atom phasing model consistent with the proposed structure.[22] All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97).[23] All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. Crystallographic data are summarized in Table 1, and an ORTEP representation of one unit is shown in Figure 1.

Results and Discussion

$[Cr^{III}F(NCMe)_5](BF_4)_2 \cdot MeCN$, 1. Complex **1** is unexpectedly formed on long standing of $[Cr^{III}(NCMe)_6](BF_4)_3$ in MeCN. This is noted as the orange solution turns dark purple, and **1** was isolated after ~72 h. The presence of fluoride in **1** is attributed to the dissociation of BF_4^- in MeCN to give F^- and $BF_3 \cdot MeCN$[24] and has been previously observed in the formation of a $Cr^{III}-F$ bond and $BF_3 \cdot Solv$ (Solv = THF) by Cotton and co-workers.[25] While not a common fluoride source, fluoride abstraction from BF_4^- has

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been reported in several other circumstances.[26,27] Complex **1** loses MeCN easily, and TGA/MS showed six molecules of MeCN being lost (50.68% mass loss) for **1** between 50 and 200 °C, which was then followed by decomposition at higher temperatures (Figure S1, Supporting Information).

The structure of **1** was determined to have a [Cr^{III}F(NCMe)$_5$](BF$_4$)$_2$·MeCN composition by single-crystal X-ray analysis. The crystallographic data are summarized in Table 1, and an ORTEP drawing is shown in Figure 1. The 1.8121(9) Å Cr−F bond distance is shorter than that found in [Cr^{III}F$_6$]$^{3-}$ (1.90 Å),[28] suggesting that the Cr^{III}−F bond is stronger in **1** than in [Cr^{III}F$_6$]$^{3-}$, and is in agreement with previously reported literature ranges of Cr^{III}−F bond lengths (1.802−1.930 Å).[1e–g] The equatorial Cr−N bond lengths range from 2.0109(14) to 2.0242(14) Å with an average value of 2.0153(14) Å. The average equatorial Cr−N bond length is shorter than the axial Cr−N bond distance of 2.0555(14) Å as a result of being trans to the fluoride atom. The trans position of the electron-withdrawing fluorine atom pulls electron density from the Cr^{III}, decreasing its π-backbonding ability to the π* orbital of the nitrile ligand. This ultimately results in an elongation of the axial Cr−N bond distance observed from the structural data. All of the Cr−N−C bond angles are less than the ideal 180°, with equatorial bond angles ranging from 171.23(13) to 174.63(13)° and averaging 172.6°, while the axial Cr−N−C bond angle is 169.34(13)°. In the unit cell, there are also two tetrahedral BF$_4^-$ anions and one noncoordinated MeCN solvent molecule.

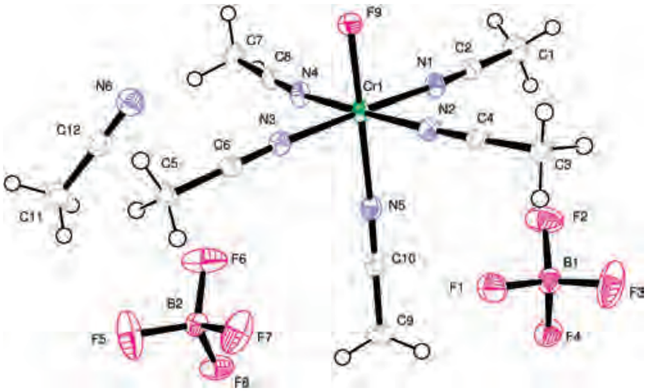

Figure 1. ORTEP (50%) atom labeling diagram of [Cr^{III}F(NCMe)$_5$](BF$_4$)$_2$·MeCN, **1**.

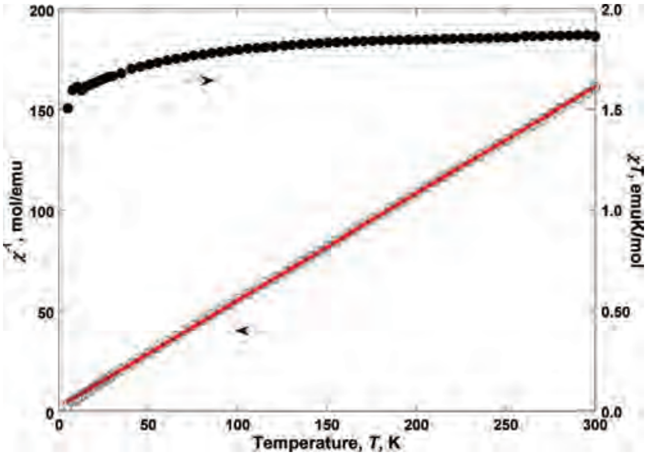

Figure 2. Temperature dependence of χT (●) and χ^{-1} (○) of **1** at 500 Oe (fit of χ^{-1} is the solid line).

In the solid state, **1** exhibits three ν_{NCMe} absorptions, two strong absorptions at 2305 and 2332 cm^{-1} corresponding to coordinated MeCN and one weak absorption at 2252 cm^{-1} which corresponds to noncoordinated MeCN. These coordinated ν_{NCMe} absorptions are almost identical to the 2301 and 2331 cm^{-1} absorptions observed for [Cr^{III}(NCMe)$_6$](BF$_4$)$_3$.[11] The IR spectra of these two compounds are almost identical, with the exception of the additional strong absorption at 640 cm^{-1} being observed for **1** (Figure S3, Supporting Information). This absorption is assigned to the Cr−F stretching mode and falls within the range of reported terminal M−F stretching frequencies (500−750 cm^{-1}).[29] The electronic spectrum (10 000−35 000 cm^{-1}) of **1** in a MeCN solution is comprised of two absorptions at 17 470 cm^{-1} (λ = 573 nm, ε = 35 M^{-1}cm^{-1}) and 23 330 cm^{-1} (429 nm, 30 M^{-1}cm^{-1}; Figure S4, Supporting Information). These bands are red-shifted ~17% relative to that of the absorptions previously reported for [Cr^{III}(NCMe)$_6$](BF$_4$)$_3$, where absorptions at 20 160 cm^{-1} (λ = 496 nm, ε = 33 M^{-1}cm^{-1}) and 27 470 cm^{-1} (364 nm, 32 M^{-1}cm^{-1}) are observed (Figure S4, Supporting Information).[11] This ~17% shift corresponds to the six MeCN ligands in [Cr^{III}(NCMe)$_6$](BF$_4$)$_3$ being reduced to five MeCN ligands in **6** with a weak-field fluoride ligand replacing one of the MeCN molecules, overall lowering the ligand field splitting energy, Δ_o. From ligand field theory, Δ_o is 17 470 cm^{-1}, an average of 590 cm^{-1} greater than the 16 960 and 16 800 cm^{-1} Δ_o values reported for [Cr^{III}F(OH$_2$)$_5$]SiF$_6$[15a] and [Cr^{III}F(OH$_2$)$_5$]SO$_4$,[15b] respectively. Hence, MeCN is a stronger field ligand than H$_2$O.[10a,11] It is also noteworthy that the replacement of one MeCN by the weak-field F$^-$ ligand results in a comparable decrease (2690 cm^{-1}) in the Δ_o splitting for [Cr^{III}(NCMe)$_6$](BF$_4$)$_3$ from 20 160 cm^{-1} to 17 470 cm^{-1} for **1** to the replacement of all six MeCN's by H$_2$O (3160 cm^{-1} decrease),[11] confirming that fluoride is one of the weakest field ligands in the spectrochemical series.

The 5−300 K magnetic susceptibility, χ, of **1** has a room temperature χT of 1.87 emuK/mol, in good agreement with the spin-only value of 1.875 emu K/mol. Above 50 K, $\chi(T)$ could be fit to the Curie−Weiss expression, $\chi \propto (T - \theta)^{-1}$, with g = 2.00 and θ = −4 K (Figure 2). This g value is consistent with other reported Cr^{III} complexes with a ^4A_g ground state.[30] The negative Weiss constant, θ, corresponds to weak antiferromagnetic coupling dominating the short-range interactions.

(NEt$_4$)$_{0.04}$[Cr^{III}F]$_{1.54}$[Cr^{III}(CN)$_6$](BF$_4$)$_{0.12}$·0.10(MeCN), 2. Complex **2** is an olive green precipitate formed from the reaction of [Cr^{III}F(NCMe)$_5$](BF$_4$)$_2$·MeCN with (NEt$_4$)$_3$[Cr^{III}-

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(26) (a) Min, K. S.; Arif, A. M.; Miller, J. S. *Inorg. Chim. Acta* **2007**, *360*, 1854. (b) Gorrell, I. B.; Gerard, P. *Inorg. Chem.* **1990**, *29*, 2452. (c) Zhu, Q.; Nelson, K. J.; Shum, W. W.; DiPasquale, A.; Rheingold, A. L.; Miller, J. S. *Inorg. Chim. Acta* **2008**, *361*, [online]DOI:, 10.1016/j.ica.2008.04.015.

(27) Crabtree, R. H.; Hlatky, G. G.; Holt, E. M. *J. Am. Chem. Soc.* **1983**, *105*, 7302.

(28) Babel, D. *Z. Anorg. Allg. Chem.* **1974**, *406*, 23.

(29) Nakamoto, K. In *Infrared and Raman Spectra of Inorganic and Coordination Compounds Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1997; pp 184.

$(CN)_6]$ (3:2) in MeCN.[31] The color is in contrast to the recently reported, very similar red-brown $Cr^{III}[Cr^{III}(CN)_6]\cdot 0.16(MeCN)$.[12] Complex **2** is a new PB-like material with fluoride occupying one of the chromium's coordination sites, that is, forming $[FCr^{III}(NC\text{-}Cr^{III})_5]$ moieties, resulting in only five cyanides bridging to the $Cr^{III}-F$ species. To the best of our knowledge, this type of binding in a Prussian blue analog (PBA) has not been previously reported; however, several dinuclear complexes containing $Cr^{III}F^{2+}$ and a μ-cyano bridging ligand are reported.[18] In the solid state, **2** exhibits a broad ν_{CN} absorption at 2168 cm^{-1} (hwhh: 22 cm^{-1}; Figure S5, Supporting Information) that is slightly shifted to lower energy from that observed for $Cr^{III}[Cr^{III}(CN)_6]\cdot 0.16(MeCN)$ ($\nu_{CN} = 2173$ cm^{-1}; hwhh: 26 cm^{-1}).[12] The 2168 cm^{-1} absorption is shifted to higher energy with respect to $[Cr^{III}(CN)_6]^{3-}$ ($\nu_{CN} = 2111$ cm^{-1}).[12] This shift is consistent with that of other PB-like materials and is due to the loss of electron density from the 5s orbital and the lack of back-bonding via the N atom.[29] This value also falls in the typical range reported for $Cr^{III}F^{2+}$-containing μ-cyano ($FCr^{III}-NC-Cr^{III}$) dinuclear complexes reported by Ribas and co-workers (2160−2180 cm^{-1}).[18] In addition, **2** should have a $Cr^{III}-F$ stretching absorption in the range of 500−750 cm^{-1}; however, it cannot be unambiguously assigned, as it is likely buried under the very broad absorptions observed at 510 cm^{-1} that are ascribed to M−C and M−N stretching frequencies.[29]

Complex **2** is thermally unstable above ~50 °C, as the TGA/MS data show a rapid loss of MeCN and cyanide. Upon further heating, a continuous gradual mass loss up to 600 °C (Figure S2, Supporting Information) occurs, resulting in a black residue. Due to this gradual mass loss, which was attributed to simultaneous solvent loss and decomposition, the temperatures at which these events occurred are indistinguishable. Nevertheless, the total mass loss for **2** was determined to be 47.6%. Hence, **2** is not very thermally stable due to the facile loss of MeCN and cyanide at relatively low temperatures; therefore, it must be stored and handled at −25 °C and exposure to ambient temperatures minimized. Drying of the samples before analyses was performed at room temperature under a vacuum to avoid any thermal decomposition at elevated temperatures.

PBAs adopt a faced-centered cubic (*fcc*) structure with a lattice constant (a) ranging from 9.9 to 10.9 Å.[17,32] The diffraction pattern of **2** has weak, broad peaks indicative of being completely amorphous and could not be indexed to the *fcc* structure. Hence, **2** is amorphous and structurally disordered. This results in small sample-to-sample variations of the composition, structural, and magnetic properties. The synthesis of more crystalline samples was attempted by varying the addition rates in the reaction conditions (fast versus slow); however, all samples were concluded to be amorphous regardless of synthetic procedure.

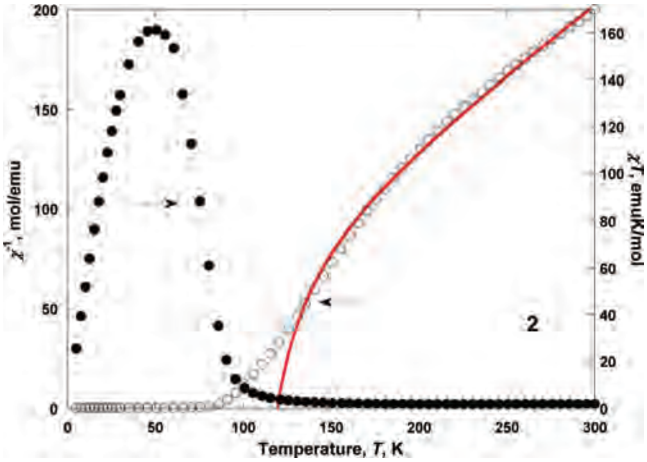

Figure 3. $\chi T(T)$ (●) and $\chi^{-1}(T)$ (○) for $(NEt_4)_{0.04}[Cr^{III}F]_{1.54}[Cr^{III}(CN)_6](BF_4)_{0.12}\cdot 0.10(MeCN)$, **2**. The fit to Néel's hyperbolic equation, eq 1, is the solid line. Samples were cooled in a zero applied field to 5 K, and data were measured upon warming in a 500 Oe applied field.

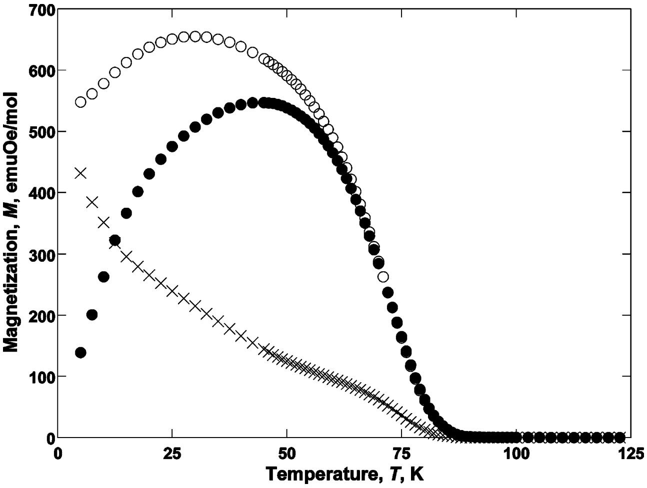

Figure 4. Five Oe $M_{ZFC}(T)$ (●) and $M_{FC}(T)$ (○) and $M_{rem}(T)$ (×) data for $(NEt_4)_{0.04}[Cr^{III}F]_{1.54}[Cr^{III}(CN)_6]-(BF_4)_{0.12}\cdot 0.10(MeCN)$, **2**.

Compex **2** has a room-temperature χT value of 1.87 emu K/mol that is substantially lower than the spin-only value of 4.76 emu K/mol (for Cr^{III}, $S = 3/2$ and $g = 2$) (Figure 3 and Figure S6, Supporting Information). Above 225 K, $\chi^{-1}(T)$ was fit to the Curie−Weiss expression with $\theta = -23$ K, indicating that moderate antiferromagnetic coupling dominates the short-range exchange. This θ value is over 2 orders of magnitude lower than that observed for strongly antiferromagnetically coupled $Cr^{III}[Cr^{III}(CN)_6]\cdot 0.16MeCN$ ($\theta = -524$ K).[12] When this observed θ value of −23 K was used, the $\chi T(T-\theta)_{calcd}$ value was calculated to be 4.42 emu K/mol, but this is still much higher than that observed at room temperature, and the genesis of this large deviation is unclear.[33]

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(30) Boudreaus, E. A.; Mulay, L. N. In *Theory and Applications of Molecular Paramagnetism*; Wiley-Interscience: New York, 1976; pp 167.

(31) While this is the best characterized composition, related materials of $(NEt_4)_a[Cr^{III}F]_{1.54}[Cr^{III}(CN)_6](BF_4)_{a+0.8}\cdot z(MeCN)$ composition were noted.

(32) (a) Ludi, A.; Güdel, H. U. *Struct. Bonding (Berlin)* **1973**, *14*, 1. (b) Dunbar, K. R.; Heintz, R. A. *Prog. Inorg. Chem.* **1997**, *45*, 283.

(33) Similar θ values have been observed for the $Cr^{III}F^{2+}$ containing *m*-cyano dinuclear species reported by Ribas and co-workers where $\theta = -25$ K was reported for *cis*-$K[(en)_2FCrNCCr(CN)_5]\cdot 2H_2O$ (en = ethylenediamine).[18b]

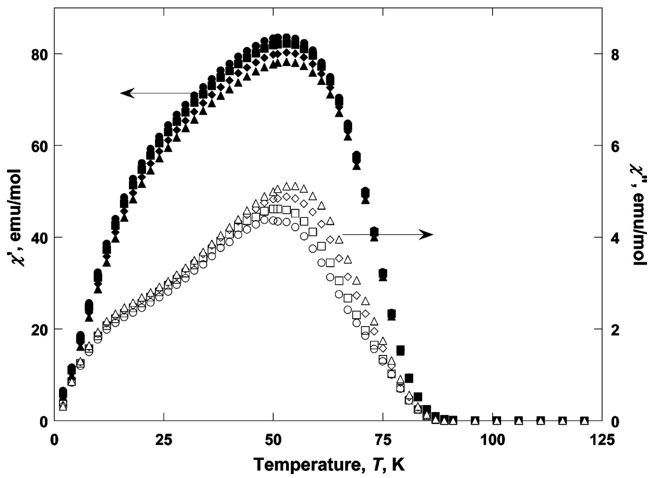

Figure 5. Observed $\chi'(T)$ (filled symbols) and $\chi''(T)$ (open symbols) for $(NEt_4)_{0.04}[Cr^{III}F]_{1.54}[Cr^{III}(CN)_6]-(BF_4)_{0.12} \cdot 0.10(MeCN)$, **2**, at 33 (circles), 100 (squares), 333 (diamonds), and 1000 (triangles) Hz at zero applied field.

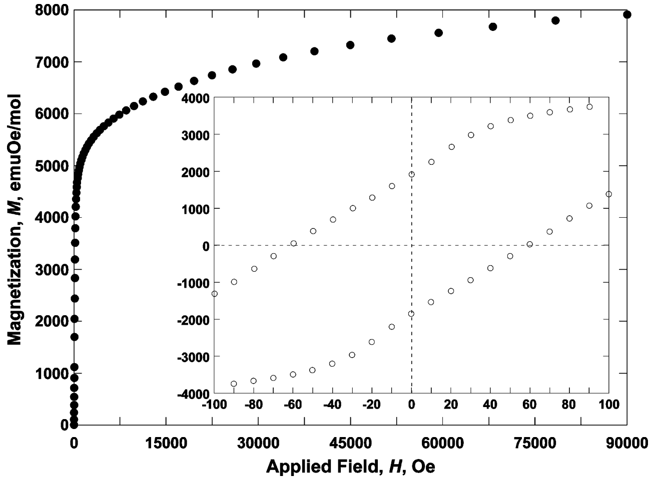

Figure 6. $M(H)$ data for $(NEt_4)_{0.04}[Cr^{III}F]_{1.54}[Cr^{III}(CN)_6](BF_4)_{0.12} \cdot 0.10$ (MeCN), **2**, at 2 K.

As the temperature is lowered, the $\chi T(T)$ of **2** gradually decreases, reaching a minimum of 1.77 emu K/mol at 220 K before gradually increasing as the temperature decreases to 100 K (Figure 3 and Figure S6, Supporting Information). Below 100 K, the $\chi T(T)$ data abruptly increase, reaching a maximum of 161 emu K/mol at 50 K, before decreasing rapidly to 25.3 emu K/mol at 5 K. This rise in $\chi T(T)$ to a maximum suggests a magnetically ordered system, and the minimum in $\chi T(T)$ observed at 220 K (above the expected ordering temperature) is consistent with a ferrimagnet and is a consequence of short-range antiferromagnetic correlations leading to a cancelation of spins.[34,35] Complex **1** is therefore a ferrimagnet where the $S = 3/2$ Cr^{III} spins couple antiferromagnetically. Above 125 K, $\chi^{-1}(T)$ was fit to the Néel hyperbolic equation, eq 1:[35]

$$\chi^{-1} = \frac{T-\theta}{C} - \frac{\zeta}{T-\theta'} \qquad (1)$$

where C and θ are the Curie and Weiss constants, respectively, and θ' and ζ are proportional to $\eta_A\eta_B C(\eta_A - \eta_B)$ and $\eta_A\eta_B C$ (where η_i is the fractional occupancy of each sublattice site), respectively, and a Néel temperature, T_N, of 120 K was obtained (Figure 3). A θ value of -23 K was obtained and is identical with the Curie–Weiss approximation, confirming moderate antiferromagnetic coupling in the high-temperature region. This value of T_N must be taken with caution because the T_N values are dependent on the lower limit of the fitted data. This is due to the odd nonhyperbolic shape of the $\chi^{-1}(T)$ data that is likely caused by the multiphase nature of these materials and can be explained by small ferrimagnetic spin domains that are well separated by a larger sea of paramagnetic spins. This is a cluster-glass behavior, and at sufficiently low temperature, these ferrimagnetic clusters will freeze in a random orientation similar to spin-glass materials.[36] The ac-susceptibility measurements confirm this hypothesis (vide infra).

Low-field $M(T)$ measurements are used to determine key information about an ordering system, and the low field $M_{ZFC}(T)/M_{FC}(T)$ for **2** shows the onset of magnetic ordering, T_{onset}, below 82 K (by extrapolation of the steepest slope to the T where $M = 0$), and the blocking temperature, T_b, is 70 K (Figure 4). T_b is the temperature at which the magnetizations of the $M_{ZFC}(T)/M_{FC}(T)$ data diverge, and below this temperature, there is a certain irreversibility (or hysteresis) in these magnetizations as a result of entering the magnetically ordered state. The decrease in magnetization below the peak in the $M_{ZFC}(T)/M_{FC}(T)$ data is consistent with this sample having antiferromagnetic interactions resulting in ferrimagnetic behavior.

The frequency-dependent real, in-phase, $\chi'(T)$ and imaginary, out-of-phase, $\chi''(T)$ components of the ac susceptibility can also be used to determine the magnetic ordering temperatures. In a zero applied dc field, **2** exhibits a response in both $\chi'(T)$ and $\chi''(T)$ with a magnetic ordering temperature of 85 K [from the initial rise in the $\chi''(T)$ data upon cooling] (Figure 5). This ordering temperature is consistent with the onset of magnetic ordering obtained from the $M_{ZFC}(T)/M_{FC}(T)$ data (82 K). Complex **2** has an observable frequency dependence, $\phi = 0.013$, which is attributed to a spin- or cluster-glass behavior.[36] Spin- or cluster-glass behavior has been reported for other PB-like materials and is indicative of a more disordered or amorphous material[37] and is consistent with the PXRD data. The temperature at which the maximum in the $\chi'(T)$ data becomes frequency-dependent

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(34) (a) Stumpf, H. O.; Pei, Y.; Kahn, O.; Sletten, J.; Renard, J. P. *J. Am. Chem. Soc.* **1993**, *115*, 6738. (b) Stumpf, H. O.; Ouahab, L.; Pei, Y.; Bergerat, P.; Kahn, O. *J. Am. Chem. Soc.* **1994**, *116*, 3866.

(35) (a) Néel, L. *Ann. Phys.* **1948**, *3*, 137. (b) Smart, J. S. *Am. J. Phys.* **1955**, *23*, 356.

(36) Mydosh, J. A. In *Spin Glasses: An Experimental Introduction*; Taylor and Francis: London, 1993, p 67.ϕ is a parameter indicative of the amount of spin disorder in a material known as spin-glass behavior: $\phi = \Delta T_{max}/[T_{max}(\Delta \log \omega)]$, where ΔT_{max} = difference between peak maximum of the temperatures at the high and low frequencies, T_{max} = peak maximum of the temperature at low frequency, $\Delta \log \omega$ = difference in the logarithms of the high and low frequencies (ω).

(37) (a) Buschmann, W. E.; Ensling, J.; Gütlich, P.; Miller, J. S. *Chem.—Eur. J.* **1999**, *5*, 3019. (b) Sendek, M.; Csach, K.; Kavecansky, V.; Lukácová, M.; Marysko, M.; Mitróová, Z.; Zentko, A. *Phys. Status Solidi A* **2003**, *196*, 225. (c) Nelson, K. J.; Giles, I. D.; Troff, S. A.; Arif, A. M.; Miller, J. S. *Inorg. Chem.* **2006**, *45*, 8922.

corresponds to the temperature at which the magnetic moments of this disordered material become frozen, and this is the freezing temperature, T_f. The T_f for **2** is determined [by the peak in the $\chi'(T)$ at 33 Hz] to be 53 K. The spin- or cluster-glass behavior supports the hypothesis that there are small ferrimagnetic domains separated by a sea of paramagnetic spins.

M(*H*) measurements at 2 K show that **2** does not saturate at 90 000 Oe where a magnetization value of 7910 emu Oe/mol is observed (Figure 6), which is reduced from 9050 emu Oe/mol, the theoretical saturation magnetization for this Cr^{III} $S = 3/2$ and $g = 2$ spin system with antiferromagnetically aligned spins. The theoretical value is approached; therefore, the magnetization at high field and low temperature is consistent with the proposed composition of $(NEt_4)_{0.04}[Cr^{III}F]_{1.54}[Cr^{III}(CN)_6](BF_4)_{0.12}\cdot 0.10(MeCN)$, whereas the $\chi T(T)$ data have larger deviations in the expected high-temperature χT values. In addition, hysteresis was also observed for **2** at 2 K (coercive field, H_{cr}, of 60 Oe) with a remnant magnetization, M_{rem}, of 1880 emu Oe/mol (Figure 6, inset).

Conclusion

$[Cr^{III}F(NCMe)_5](BF_4)_2$ has been characterized to be a source of $Cr^{III}F^{2+}$ in nonaqueous media and exhibits a crystal field splitting energy, Δ_o, of 17 470 cm^{-1}. This Δ_o is 2690 cm^{-1} lower than that observed for $[Cr^{III}(NCMe)_6](BF_4)_3$ ($\Delta_o = 20\,160$ cm^{-1}), consistent with substituting a MeCN ligand with a weaker field F^- ligand. This nonaqueous source of $Cr^{III}F^{2+}$ was used to prepare a Prussian-blue-like material of $(NEt_4)_{0.04}[Cr^{III}F]_{1.54}[Cr^{III}(CN)_6](BF_4)_{0.12}\cdot 0.10(MeCN)$ composition, which is a ferrimagnetic material with a T_c of 85 K (from ac measurements, Figure 5). An overall reduction of 18% (25 K) in the magnetic ordering temperature is observed when going from $Cr^{III}[Cr^{III}(CN)_6]\cdot 0.16(MeCN)$ to $(NEt_4)_{0.04}[Cr^{III}F]_{1.54}[Cr^{III}(CN)_6](BF_4)_{0.12}\cdot 0.10(MeCN)$ (ac results). This reduction is a result of the decrease of nearest neighbors by the introduction of the F^- ion onto the solvated metal cation. Below the ordering temperature, small ferrimagnetic domains are frozen randomly, resulting in an overall bulk response of magnetic ordering, and a T_f of 53 K is observed ($\phi = 0.013$). This glassy behavior is caused by the material being amorphous and structurally disordered, as has been reported previously for PBAs. Magnetic ordering is further confirmed by the hysteretic effect observed at 2 K, where $H_{cr} = 60$ Oe and $M_{rem} = 1880$ emu Oe/mol. Thus, $[Cr^{III}F(NCMe)_5]^{2+}$ is a precursor for the synthesis of new materials. Future studies involving the incorporation of the $[Cr^{III}F(NCMe)_5]^{2+}$ cation toward the design and synthesis of similar PB-like and other molecular materials can be exploited.

Acknowledgment. The authors gratefully acknowledge the fruitful discussions with Profs. T. G. Richmond and R. D. Ernst, as well as continued partial support from the U.S. DOE Basic Energy Sciences (Grant No. DE FG 03-93ER45504) and the AFOSR (Grant No. F49620-03-1-0175).

Supporting Information Available: Figures S1−S6 are available free of charge via the Internet at http://pubs.acs.org. CCDC-654511 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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