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Nanocomposite of a chromium Prussian blue with TiO_2. Redox reactions and the synthesis of Prussian blue molecule-based magnets

Stephen M. Holmes, Amy S. Whelpley, Gregory S. Girolami *

School of Chemical Sciences, Department of Chemistry, University of Illinois at Urbana-Champaign, 600 South Goodwin Avenue, Urbana, IL 61801, USA

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Abstract

The reaction of $[NEt_4]_3[Cr(CN)_6]$ with titanium(III) *p*-toluenesulfonate at a pH of 2 affords a gray solid whose metal content and spectroscopic and magnetic properties are fully consistent with it being a Prussian blue material of stoichiometry "$Ti^{III}[Cr^{III}(CN)_6] \cdot H_2O$". The carbon, nitrogen, and hydrogen content, however, are not consistent with this stoichiometry, and further investigation showed that the gray material has a powder X-ray diffraction profile, infrared spectrum, and magnetic properties very similar to those of the "all-chromium" Prussian blue $Cr^{II}[Cr^{III}(CN)_6]_{0.67} \cdot 6H_2O$. All data, including the C, H, and N weight percentages, are consistent with the conclusion that the material isolated is a nanocomposite of $Cr^{II}[Cr^{III}(CN)_6]_{0.67} \cdot xH_2O$ and TiO_2 in the ratio of 1–1.6. These results suggest that Ti^{III} reduces some of the $[Cr^{III}(CN)_6]^{3-}$ ions to generate Ti^{IV} and Cr^{II}; the former hydrolyzes to amorphous $TiO_2 \cdot 2H_2O$, the latter loses its bound CN ligands and reacts with unreacted $[Cr^{III}(CN)_6]^{3-}$ ions to generate the crystalline all-chromium PB species. The electrochemical potentials suggest that the $[Cr^{III}(CN)_6]^{3-}$ ion should not be reduced by Ti^{III}; evidently, this unfavorable reaction is driven by the insolubility of the reaction products. The results constitute a cautionary tale in two respects: first, that the characterization of Prussian blue materials must be conducted with care and, second, that the insolubility of Prussian blue analogues can sometimes drive reactions that in solution are thermodynamically unfavorable.

Keywords: Prussian blue; Titanium dioxide; Hexacyanometalate; Magnetic; Hydrolysis; Redox; Nanocomposite

1. Introduction

In the 1990s, an entirely new class of room temperature magnetic solids was discovered: these molecule-based magnets are constructed by molecular self-assembly strategies, rather than ceramic and metallurgical techniques commonly utilized for the preparation of oxide- and alloy-based magnets. Two subclasses of room-temperature molecule-based magnets are currently known, both of which contain low-valent early transition metal centers: Prussian blue materials [1–3], and certain metal salts of cyanoalkene radical anions [4,5]. Molecule-based magnets often exhibit fascinating and unprecedented bulk properties such as photo-induced magnetism because the materials combine aspects of both molecular and extended solids [6]. As a result, molecule-based magnets hold promise as new smart materials for a variety of twenty-first century applications such as energy efficient and fast photonic or spintronic computing systems and memory devices.

The ability of certain Prussian blue analogues to exhibit spontaneous bulk magnetization at high temperatures can be ascribed to their three-dimensional nature and the efficient superexchange that occurs by means of the cyanide ligands, which link adjacent metal centers by means of M(μ-CN)M′ bridges. Owing to the asymmetry of the cyanide linker, the metal centers in the Prussian blue structure are of two types: those attached to the carbon end of the

* Corresponding author. Tel.: +1 217 333 2729; fax: +1 217 244 3186.
E-mail address: girolami@scs.uiuc.edu (G.S. Girolami).

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CN linker, and those attached to the nitrogen end. The superexchange mechanism in these solids involves delocalization of spin density via π backbonding of unpaired t_{2g} electrons from the metals in the carbon sites into the bridging cyanide π^* orbitals; more efficient delocalization typically leads to larger exchange couplings (J) and higher magnetic ordering temperatures (T_C or T_N). The magnetic ordering temperatures of Prussian blue analogues can be maximized by constructing them from metal centers bearing electrons in high-energy d-orbitals: such centers are capable of back bonding strongly into the cyanide π^* orbitals and maximizing the extent of spin delocalization [7–9].

For hexacyanometalate ions of first-row transition metals, the energies of the d-electrons depend on two parameters. The first of these parameters is the oxidation state of the metal. Metals in lower oxidation states have more electrons to screen the nuclear charge, and the increased screening leads to an increase in the energies of all the valence electrons. Although hexacyanometalates are known in the +1 oxidation state, all are diamagnetic and thus ill-suited for preparing Prussian blue magnets; the lowest oxidation state accessible for paramagnetic hexacyanometalate ions is +2. The second parameter that controls the energies of the d-electrons is the position of the metal in the first-row of the periodic table. Other things being equal, metals early in the d-block have higher-energy d-electrons because they have lower nuclear charges. This fact explains why the highest ordering temperatures seen to date are for Prussian blue analogues that contain vanadium(II) centers: early transition metal ions in low oxidation states have electrons in high-energy, radially expanded d-orbitals, and these electrons delocalize quite readily into the cyanide π^* orbitals, thus increasing the exchange coupling between adjacent spin centers, and affording magnetic materials with higher magnetic ordering temperatures.

Because substitution of early transition metals into the Prussian blue structure gives magnets with unusually high ordering temperatures, we have long been interested in preparing a Prussian blue analogue that contains the earliest first-row transition metal, titanium. In 1997, we described the synthesis of the hexacyanotitanate(III) ion, and had high hopes for preparing new magnets from this building block in which the Ti^{III} center occupied the carbon sites of the Prussian blue structure [10]. Unfortunately, all attempts to prepare magnetic phases from this starting material have been unsuccessful. The $[Ti^{III}(CN)_6]^{3-}$ ion is instantly hydrolyzed in water, so this medium cannot be used for the synthesis of Prussian blue analogues from this starting material. Although the $[Ti^{III}(CN)_6]^{3-}$ ion is soluble in acetonitrile, and its solutions afford precipitates upon the addition of transition metal cations such as V^{II}, Cr^{II}, or Mn^{II}, the solids obtained are non-crystalline and non-magnetic, probably because the precipitation is rapid and irreversible in this poorly coordinating solvent, so that there is no opportunity for an ordered Prussian blue structure to form [6].

In the present study, we report our attempts to prepare Prussian blues in which the titanium(III) center is not in the carbon site, but rather in the nitrogen site of the PB structure. Despite the fact that the titanium(III) center carries only one unpaired electron, so that few spin exchange pathways are available, the low value of the effective nuclear charge of the titanium(III) ion means that this electron will reside in a very high energy d-orbital. As a result, incorporating Ti^{III} into a PB should afford solids with high magnetic ordering temperatures because the one d-electron should delocalize significantly into the cyanide π^* orbital.

The high energy of the d-orbitals on titanium(III) ion means that it is a strong reductant, a fact that is well known from its electrochemistry and solution reaction chemistry. Thus, in order to use this cation as a starting material for the synthesis of Prussian blues, we chose to investigate its reactions with an anion that is relatively difficult to reduce: the hexacyanochromate(III) ion $[Cr(CN)_6]^{3-}$. The redox potentials suggest that these two reactants should not undergo a redox reaction. We find that these two building blocks do react to generate a Prussian blue phase, but not one containing both titanium and chromium. Instead, the product has been identified as a nanocomposite of titanium dioxide with an all-chromium Prussian blue. Such nanocomposites have recently been shown to be useful in the construction of photoelectrodes [11].

2. Results and discussion

2.1. Attempts to synthesize titanium(III) hexacyanochromate(III) in water

We began our investigations with the reaction of titanium(III) ions with hexacyanometalates in aqueous solutions. The hexaaquotitanium(III) ion is known to be stable in water only if the pH is kept below ~1 [12]. At higher pH values, the hexaaqua ion undergoes ionization reactions to produce $[Ti^{III}(OH)(OH_2)_5]^{2+}$ and other, more highly condensed species. Therefore, we dissolved titanium(III) *p*-toluenesulfonate in water that had been acidified to pH ~2 with *p*-toluenesulfonic acid, and to this solution we added $[NEt_4]_3[Cr(CN)_6]$. From the mixture, we isolated a gray solid, which was isolated by centrifugation, washing, and drying; we will refer to this product as **1**. The metal weight percentages (Cr, 19.4; Ti, 17.4) were consistent with those calculated (Cr, 19.0; Ti, 17.5) for the molecular formula "$Ti[Cr(CN)_6] \cdot H_2O$".

The X-ray powder diffraction pattern of **1** contains several peaks, all of which can be indexed to a face-centered cubic cell with a lattice constant of 10.36 Å (Fig. 1). The symmetry of the cell and its cell parameters are strongly indicative of the presence of a Prussian blue phase. The average crystallite size, which was estimated from the widths of the diffraction peaks using the Debye–Scheerer equation [13], is 224 Å.

The infrared spectrum of **1** features a single intense cyanide stretching absorption at 2181 cm^{-1}. The shifting

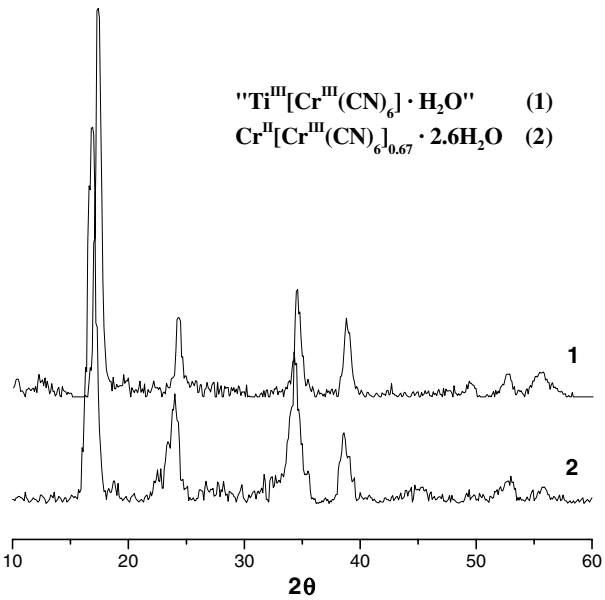

Fig. 1. Base-line-corrected powder X-ray diffraction patterns of **1** (top) and **2** (bottom). The seven main peaks are the 200, 220, 400, 420, 440, 442, and 620 reflections (left–right).

of the ν_{CN} stretching absorption to higher energies relative to that of 2112 cm^{-1} in $[NEt_4]_3[Cr(CN)_6]$ is diagnostic for the formation of cyanide groups that bridge between two metal centers. The frequency lowering is the consequence of the depopulation of the cyanide 5σ orbital upon formation of a bond between the nitrogen atom and a second metal center [14].

For Prussian blue analogues, (and other magnetic solids constructed from two interpenetrating lattices), the sign of the local exchange interactions can usually be determined from the shape of the μ_{eff} versus T curve: for ferrimagnetic solids there is a minimum in μ_{eff} above the ordering temperature owing to the effects of short-range antiferromagnetic correlations that cancel spins [15–19]. Such a minimum is observed in **1** and thus it is clearly a ferrimagnet (Fig. 2). The minimum is rather shallow and appears at *ca.* 325 K. At lower temperatures, the magnetic moment increases dramatically as the magnetic ordering temperature is approached Fig. 2.

The magnetic ordering temperature can be deduced from plots of χ^{-1} versus T (Fig. 3). The curve can be fit to Néel's hyperbolic equation, $1/\chi = (T-\theta)/C - \zeta/(T-\theta')$, where θ and C are the Weiss and Curie constants, and θ' and are 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 [20,21]. The sign of the Weiss constant is negative; this feature is characteristic of ferrimagnets. The intersection of the hyperbola with the temperature axis gives the magnetic ordering temperature (T_N). The derived value for **1** is 265 K, although a slightly different value was determined from the magnetization curves (see below), and the Weiss and Curie constants are provided in Table 1.

At 350 K, the magnetic moment per formula unit (reckoned according to the formula given above) is 4.50 μ_B and this value suggests that **1** is composed of $S = {}^3/_2$ Cr^{III} and $S = {}^1/_2$ Ti^{III} metal centers in a 1:1 ratio: the value of μ_{eff} calculated for randomized Ti^{III} and Cr^{III} spins with $g = 2$ is 4.52 μ_B.

The temperature dependence of the field-cooled, zero-field cooled, and remnant magnetization for **1** clearly show the onset on long-range magnetic order at 255 K (Fig. 4); the ordering temperature is the point at which the field-cooled and zero-field curves diverge, and also the point at which the magnetization goes to zero. The magnetic ordering temperature defined in this way is more accurate than that deduced from the χ^{-1} versus T curve.

The magnetization value of **1** (Table 1) at 5 K is 5.0 kG cm^3 mol^{-1} (again, for the formula unit given above) at an applied magnetic field of 70 kG (Fig. 5). The magnetization has not saturated even at 70 kG, but if we extrapolate to large fields, we can estimate that the saturation magnetization should be near 11 kG cm^3 mol^{-1}. For the formula "$Ti[Cr(CN)_6] \cdot H_2O$," the calculated saturation magnetization for antiferromagnetically coupled Ti^{III} and Cr^{III} centers is 11.2 kG cm^3 mol^{-1}. Compound **1**

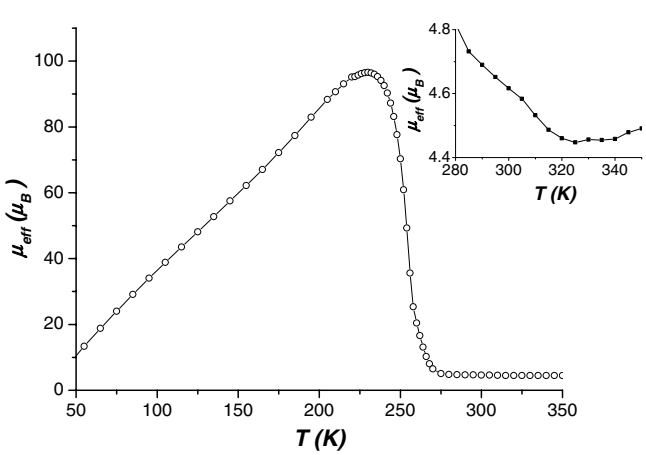

Fig. 2. Temperature dependence of the effective moment per formula unit for **1** at $H_{dc} = 25$ G. Inset: μ_{eff} vs. T plot near *ca.* 325 K.

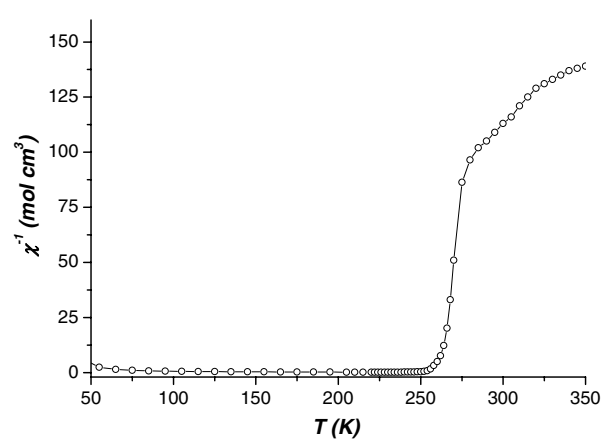

Fig. 3. Temperature dependence of the reciprocal susceptibility of **1** at $H_{dc} = 25$ G.

Table 1
Structural and magnetic data for the new hexacyanochromates

Compound	a (Å)	T_N (K)	C[a]	θ (K)	M_{sat}[b]
"$Ti^{III}[Cr^{III}(CN)_6] \cdot H_2O$ (**1**)"	10.36	255	3.95	−240	5.00
$Cr^{II}[Cr^{III}(CN)_6]_{0.66} \cdot 2.6H_2O$ (**2**)	10.44	242	2.76	−100	5.17

[a] $cm^3\ K\ mol^{-1}$.
[b] $kG\ cm^3\ mol^{-1}$ at 5 K.

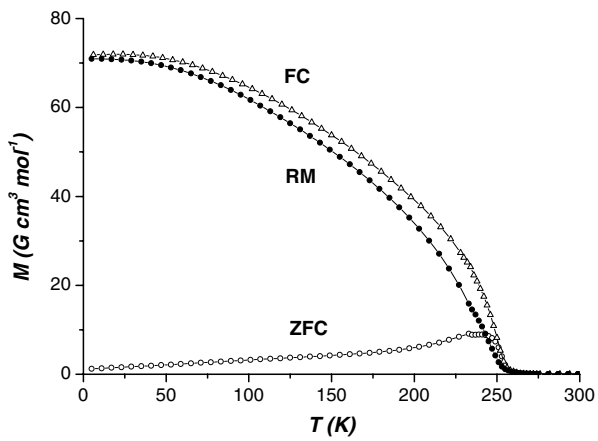

Fig. 4. Temperature dependence of the zero-field cooled (ZFC, ○), field-cooled (FC, △) and remnant magnetization (RM, ●) curves for **1** at $H_{dc} = 1$, 1, and 0 G, respectively.

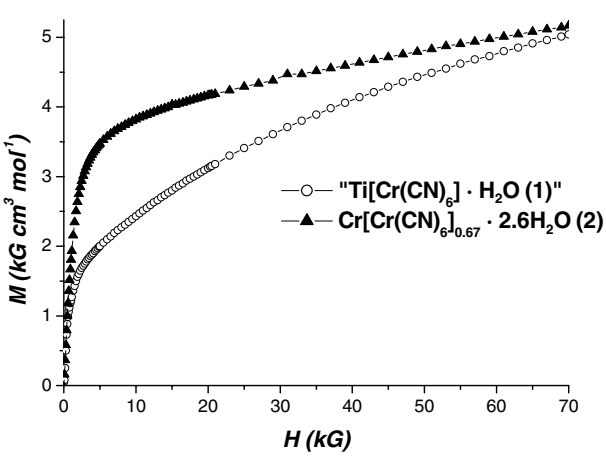

Fig. 5. Field dependence of the magnetization for **1** (○) and **2** (▲) at 5 K.

also exhibits hysteresis below its magnetic ordering temperature (Fig. 6). The coercive field measured at 5 K is 260 G (Table 2).

To summarize the results above, the metal content and all the spectroscopic data suggested that **1** was the first Prussian blue magnet containing Ti^{III}. One measurement was inconsistent with this conclusion, however: the experimentally determined carbon, hydrogen, and nitrogen analyses (C, 8.75; H, 2.49; N, 14.0) disagreed with those calculated for the formula "$Ti[Cr(CN)_6] \cdot H_2O$" (C, 26.3; H, 0.74; N, 30.7). We, therefore, were forced to reconsider

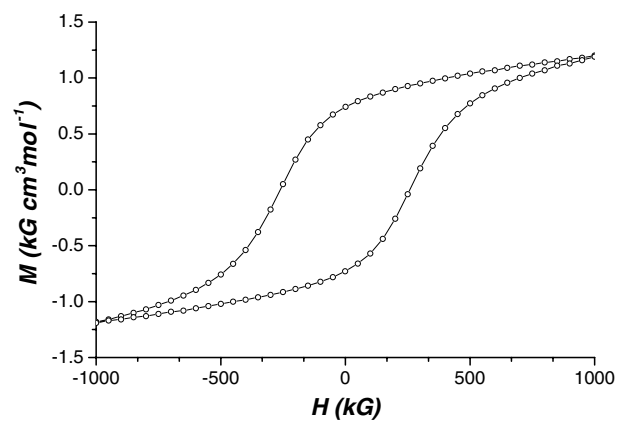

Fig. 6. Hysteresis of **1** at 5 K.

our findings about the nature of **1**. Before we discuss our conclusions, we describe a related Prussian blue compound that will be relevant to this discussion.

2.2. Synthesis and characterization of a chromium(II) hexacyanochromate(III)

Combining aqueous solutions of chromium(II) *p*-toluenesulfonate and $[NEt_4]_3[Cr(CN)_6]$ immediately affords a red-brown suspension from which an air sensitive red-brown solid of stoichiometry $Cr^{II}[Cr^{III}(CN)_6]_{0.67} \cdot xH_2O$ (**2**) can be isolated ($x \sim 2.6$).

The infrared spectrum of **2** exhibits an intense cyanide stretching band at 2180 cm^{-1}, and the high frequency of this band clearly suggests that the bridging cyanide ligands are C-bound to Cr^{III} centers. A weaker low frequency band at 2075 cm^{-1} is most likely due to cyanide groups C-bound to Cr^{II}. The powder X-ray diffraction pattern can be indexed to a face-centered cubic cell having a cell constant of 10.44(4) Å (Fig. 1). The average crystallite size, which was estimated using the Debye–Scheerer equation [13], is 102 Å.

As judged from the temperature dependence of the magnetization of **2** in an applied field of 1 G, the magnetic ordering temperature is 242 K (Figs. 7 and 8). At this temperature, the field-cooled (1 G) and zero-field-cooled (1 G) curves diverge and the remnant magnetization curve goes to zero. A fit of the χ^{-1} versus T plot (25 G) to Néel's hyperbolic function gives an essentially identical value for the magnetic ordering temperature of 237 K. The hysteresis curve for **2** is shown in Fig. 9.

Table 2
Remnant magnetizations and coercive fields for the new molecular magnets at 5 K; estimation of exchange coupling parameters (J) from the observed magnetic ordering temperatures

Compound	M_r (G cm^3 mol^{-1})	H_C (G)	J (cm^{-1})	T_N (K)
"$Ti^{III}[Cr^{III}(CN)_6] \cdot H_2O$ (**1**)"	753	260	−57	255
$Cr^{II}[Cr^{III}(CN)_6]_{0.66} \cdot 2.6H_2O$ (**2**)	760	275	−36	242

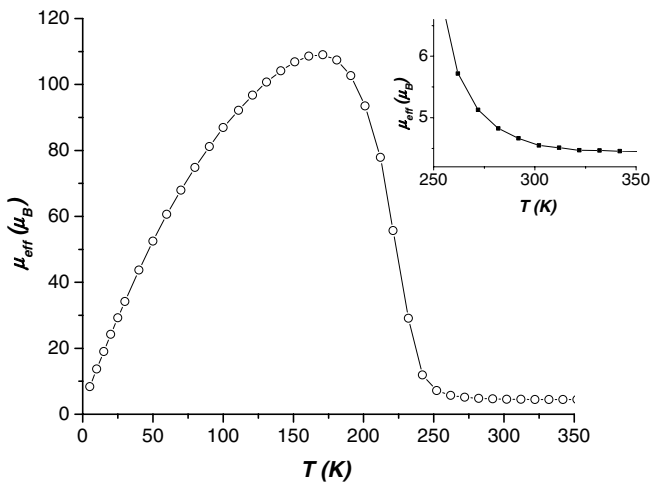

Fig. 7. Temperature dependence of **2** at $H_{dc} = 25$ G. Inset: minimum observed at *ca.* 300 K. on cooling from the high temperature limit.

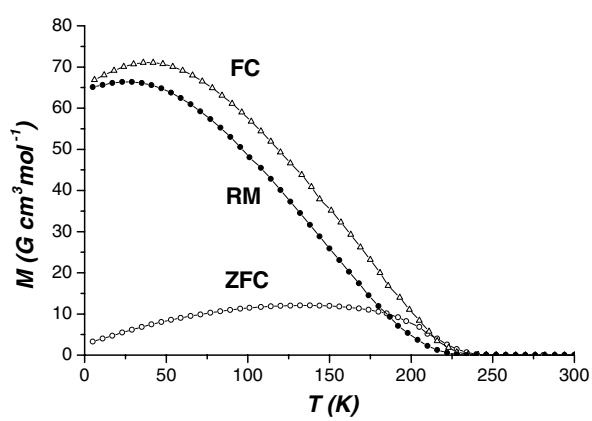

Fig. 8. Temperature dependence of the zero-field cooled (ZFC, ○), field-cooled (FC, △), and remnant magnetization (RM, ●) for **2** at $H_{dc} = 1$, 1, and 0 G, respectively.

The measured saturation magnetization of 5.17 kG cm^3 mol^{-1} (5 K, 70 kG) suggests that about half of the Cr^{II} ions are low spin and the other half are high spin, but that both types of Cr^{II} centers are coupled antiferromagnetically to the Cr^{III} center (Fig. 5). Specifically, if all of the low-spin Cr^{II} ions were low spin, then the saturation magnetization would be 0.056 kG cm^3 mol^{-1}, whereas if all of the Cr^{II} ions were high spin, then the saturation magnetization would be 11.1 kG cm^3 mol^{-1}. The slow approach to saturation could mean that **2** is a canted antiferromagnet or that it has some spin glass character [22,23]. Verdaguer has reported a similar distribution of both low and high

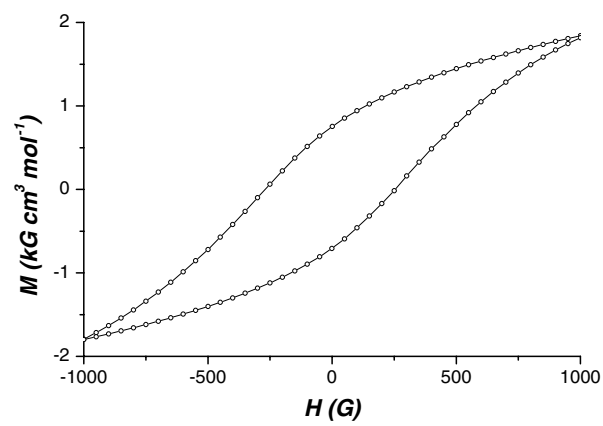

Fig. 9. Hysteresis for **2** at 5 K.

spin Cr^{II} centers in the solid $Cs_{0.75}Cr_{1.025}[Cr(CN)_6] \cdot 5H_2O$ [24].

The plot of the magnetic moment versus temperature (μ_{eff} versus T) at 25 G does not exhibit the shallow minimum just above T_N that is expected for a ferrimagnetic material (Fig. 7). It is possible that this minimum is located above 350 K, the upper limit of our data set. The observed value of the magnetic moment at room temperature (4.66 μ_B at 292 K and 4.547 μ_B at 320 K) again suggests that both low- and high-spin Cr^{II} centers are present: if all had been low-spin, then μ_{eff} should be ~4.25 μ_B, whereas if all had been high-spin, then μ_{eff} should be ~5.84 μ_B.

Verdaguer has described a similar reaction, using $CrCl_2$ as the Cr^{II} source, and has formulated the gray product as $Cr_5(CN)_{12} \cdot 10H_2O$ (or, equivalently, $Cr[Cr(CN)_6]_{0.67} \cdot 3.3H_2O$) [24]. In addition, Miller and Hashimoto have reported that thin films of mixed Cr^{II}/Cr^{III} cyanometalates, can be prepared from $CrCl_3$ and $K_3[Cr(CN)]_6$ at negative applied potentials [25–28]. Also described by Verdaguer is the green all-Cr^{II} compound $Cs_{0.75}Cr_{1.025}[Cr(CN)_6] \cdot 5H_2O$, which exhibits IR absorptions at 2187 and 2069 cm^{-1}, and is ferromagnetic below $T = 190$ K [24].

2.3. Reformulation of *1*

As mentioned above, treatment of $[Ti(OH_2)_6]^{3+}$ with $[Cr(CN)_6]^{3-}$ in water affords a gray solid whose spectroscopic properties and metal content were entirely consistent with it being a Prussian blue analog of stoichiometry $Ti[Cr(CN)_6] \cdot H_2O$. However, this formulation is inconsistent with elemental analysis carbon, hydrogen, and nitrogen values expected for **1**; several lines of evidence suggest that it is not a Prussian blue analogue containing

Ti^{III}. (1) The XRD pattern of **1** (which can be indexed to a fcc cell with a cell constant of 10.36 Å) is almost identical to the 10.44 Å value seen for $Cr^{II}[Cr^{III}(CN)_6]_{0.67} \cdot xH_2O$. The absence of peaks due to the TiO_2 component is consistent with the known behavior of nanophase titania, which generally remains amorphous until heated to temperatures above 250 °C [29]. (2) The infrared spectrum of **1** (which contains a strong absorption at 2180 cm^{-1} and a weaker broad absorption at 2075 cm^{-1}) closely resembles that of the all-chromium complex $Cr^{II}[Cr^{III}(CN)_6]_{0.67} \cdot xH_2O$. The presence of TiO_2 is signaled by the IR band at 800 cm^{-1}, which is assigned to the longitudinal optical (LO) mode of the Ti-O bonds in rutile, which appears at 806 cm^{-1} [30]. (3) The magnetic ordering temperature ($T_N = 255$ K) for **1** is close to the magnetic phase transition temperature ($T_N = 242$ K) for $Cr^{II}[Cr^{III}(CN)_6]_{0.67} \cdot xH_2O$.

These facts strongly suggest that **1** is a mixture of $Cr^{II}[Cr^{III}(CN)_6]_{0.67} \cdot xH_2O$ and some other titanium-containing phase. In fact, all the properties of **1**, including the microanalytical data, are consistent with the conclusion that it is a mixture of $Cr^{II}[Cr^{III}(CN)_6]_{0.67} \cdot xH_2O$ and $TiO_2 \cdot nH_2O$ in the ratio of 1–1.6.

These results suggest that Ti^{III} reduces $[Cr^{III}(CN)_6]^{3-}$ to generate Ti^{IV} and Cr^{II}. The electrochemical potentials for $[Cr(CN)_6]^{3/4-}$ (−1.140 V versus SHE) [31], and Ti^{3+}/TiO^{2+} (0.008 V versus NHE) [32,33] suggest that the $[Cr^{III}(CN)_6]^{3-}$ ion should not be reduced by Ti^{III}. Of course, there will be some equilibrium concentration of the redox products of this reduction; we hypothesize that the hexaquotitanium(III) ion reduces some of the $[Cr^{III}(CN)_6]^{3-}$ ions to Cr^{II}; the latter ion is kinetically labile and will lose its CN ligands, thus providing the source of aquated Cr^{II} ions necessary to produce $Cr^{II}[Cr^{III}(CN)_6]_{0.67} \cdot x\ H_2O$. In this process the Ti^{3+} ions are oxidized to Ti^{4+}, which in aqueous solutions at low pH will generate hydrated $TiO_2 \cdot nH_2O$ [33].

2.4. Attempts to synthesize titanium(III) hexacyanochromate(III) in methanol

Treatment of $[NEt_4]_3[Cr(CN)_6]$ with $Ti(OTs)_3$ in methanol affords a dark purple suspension which slowly becomes a gel over 24 hours. The solid was collected after 3 days by centrifugation and washed with methanol to afford a dark blue solid. Consistent with the results described above, our characterization of this solid strongly suggests that it is best formulated not as a mixed Ti–Cr Prussian blue, but rather as the biphasic material $Cr[Cr(CN)_6]_{0.67} \cdot 7MeOH \cdot 1.67TiO_2$, **3**. Its XRD pattern is consistent with a fcc unit cell with a cell constant essentially identical to that described above for **1**, but the material is less crystalline, as judged from the widths of its diffraction peaks. This difference is not unexpected, because water is a better solvent than methanol, and should better facilitate the annealing out of defects in the structure as it is assembled from solution during the synthesis. The infrared spectrum of **3** exhibits an intense cyanide stretching absorption at 2168 cm^{-1} that is lower than that of 2181 cm^{-1} observed for **1**, but still consistent with the presence of $[Cr^{III}(CN)_6]^{3-}$ centers in which the CN ligands bridge to another metal center. The magnetic ordering temperature for **3** (54 K; Fig. 10) is lower than the ordering temperature observed for **1**, probably because the PB component is less crystalline.

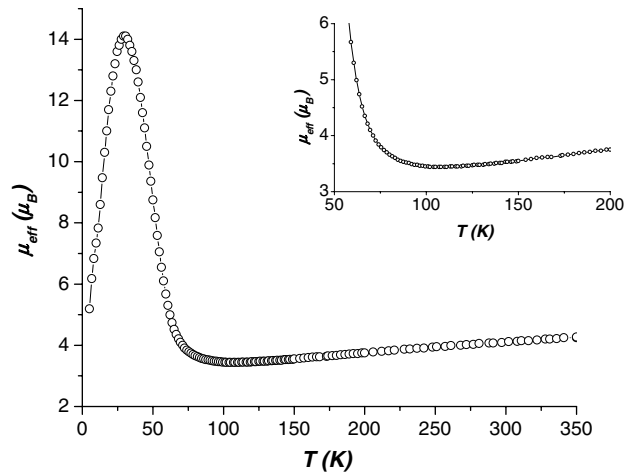

Fig. 10. Temperature dependence of the effective moment per formula unit for $Cr^{II}[Cr^{III}(CN)_6]_{0.67} \cdot 7MeOH \cdot 1.67TiO_2$ (**3**) in an applied field of 25 G. The inset shows the minimum observed near 80 K on cooling from the high temperature limit.

3. Experimental

3.1. General considerations

All operations were conducted in vacuum or under an argon atmosphere by using standard Schlenk techniques. Transfers of solutions containing cyanide were carried out through teflon cannulas. Solvents were distilled under dinitrogen from CaH_2 (acetonitrile), Mg turnings (methanol), or sodium-benzophenone (diethyl ether) and sparged with argon before use. Deionized water was sparged with argon. The salts $Cr(OTs)_2$, $Ti(OTs)_3$, and $[NEt_4]_3[Cr(CN)_6]$ are described elsewhere [34,35]. The IR spectra were recorded as Nujol mulls between KBr plates on a Perkin–Elmer 1600 FTIR instrument. Magnetic measurements were conducted on Quantum Design MPMS and $MPMS^2$ SQUID magnetometers. Diamagnetic corrections were estimated using Pascal's constants [36]: $\chi_{dia} = -150 \times 10^{-6}\ cm^3\ mol^{-1}$ for **1** and $-108 \times 10^{-6}\ cm^3\ mol^{-1}$ for **2**. Microanalyses were performed by the University of Illinois Microanalytical Laboratory. Powder diffraction measurements were carried out on a Bruker P4RA/GADDS wide angle diffractometer using a Cu Kα radiation source.

3.2. $Ti[Cr(CN)_6] \cdot H_2O$ (1)

To a solution of $Ti(OTs)_3$ (0.51 g, 0.908 mmol) and $HOTs \cdot H_2O$ (0.06 g, 0.315 mmol) in water (20 mL) was

added a solution of $[NEt_4]_3[Cr(CN)_6]$ (0.50 g, 0.835 mmol) in water (20 mL) over 10 s, affording an orange solution. After 10 min, a gray solid precipitated and the mixture was centrifuged at 3000 r.p.m. for 10 min. The supernatant was discarded and the gray solid was washed with water (2 × 40 mL), centrifuging and discarding the supernatant each time. The gray solid was washed with acetonitrile (15 mL) and was dried under vacuum at room temperature overnight. Yield: 0.094 g (34%). *Anal.* Calc. for $Ti[Cr(CN)_6] \cdot H_2O$ ($C_6H_2N_6OCrTi$): Cr, 19.0; Ti, 17.5. Found: C, 8.75; H, 2.49; N, 14.0; Cr, 19.4; Ti, 17.4%. *Anal.* Calc. for $Cr[Cr(CN)_6]_{0.67} \cdot 7H_2O \cdot 1.67TiO_2$ ($C_4H_{12}N_4O_{9.33}Cr_{1.67}Ti_{1.67}$): Cr, 19.2; Ti, 17.8. IR (cm^{-1}): 3270 (vs), 2181 (s), 2069 (w), 1614 (w), 1305 (w), 1261 (m), 1151 (m), 1074 (m), 1023 (m), 800 (vs), 525 (vs, br).

3.3. $Cr[Cr(CN)_6]_{0.67} \cdot 2.6H_2O$ (2)

To a solution of $[NEt_4]_3[Cr(CN)_6]$ (0.30 g, 0.501 mmol) in water (20 mL) was added a solution of $Cr(OTs)_2 \cdot 3.2H_2O$ (0.39 g, 0.863 mmol) in water (10 mL) over 25 s to afford a fine red-brown suspension. The mixture was transferred to an argon-filled centrifuge bottle and was centrifuged at 3000 r.p.m. for 10 min. The pale red supernatant was discarded and the brown solid was washed with water (2 × 50 mL), centrifuging and discarding the supernatant each time. The solid was then suspended in acetonitrile (20 mL) and the slurry was transferred to a flask. The solvent was removed in vacuum and the red-brown solid was dried for 10 h in vacuum at room temperature. Yield: 0.068 g (38%). *Anal.* Calc. for $Cr[Cr(CN)_6]_{0.67} \cdot 2.\ 6H_2O$: C, 20.3; H, 2.20; N, 23.6; Cr, 36.5. Found: C, 20.8; H, 2.56; N, 18.1; Cr, 36.5%. IR (cm^{-1}): 3606 (s, br), 3302 (s, br), 3192 (s, br), 2180 (s), 2075 (w), 1623 (w), 530 (s).

3.4. Attempts to synthesize titanium(III) hexacyanochromate(III) in methanol

To a solution of $[NEt_4]_3[Cr(CN)_6]$ (0.30 g, 0.501 mmol) in methanol (10 mL) was added a solution of $Ti(OTs)_3$ (0.31 g, 0.561 mmol) in methanol (10 mL). The initially dark purple suspension slowly became a gel over the course of one day. After 3 days, the dark blue solid was transferred to an argon-filled centrifuge bottle washing with methanol (5 mL) and centrifuged. The clear supernatant was discarded and the blue solid was washed with xmethanol (2 × 35 mL), centrifuging and discarding the clear supernatant each time. The solid was transferred to a flask by washing with methanol (25 mL). The solvent was removed under vacuum and the blue solid was dried under vacuum overnight. Yield: 0.127 g (89%). *Anal.* Calc. for $Cr[Cr(CN)_6]_{0.67} \cdot 7MeOH \cdot 1.67TiO_2$; $C_{11}H_{28}N_4O_{10.34}Cr_{1.67}Ti_{1.67}$: C, 24.0; H, 5.09; N, 10.2; Cr, 15.8; Ti, 14.9. Found: C, 27.0; H, 3.88; N, 12.8; Cr, 16.7; Ti, 14.9. IR (cm^{-1}): 2168 (vs), 1121 (s), 1078 (s), 1033 (s), 605 (s, sh), 504 (vs, br).

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