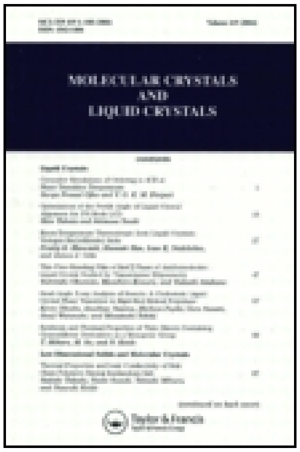

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New Prussian Blue Analogues Constructed from the $[Cr(CN)_5NO^{3-}]$ and $[Cr(CN)_6{}^{4-}]$ Anions. A Building Block Approach to High T_N Ferrimagnets

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NEW PRUSSIAN BLUE ANALOGUES CONSTRUCTED FROM THE $[Cr(CN)_5NO^{3-}]$ AND $[Cr(CN)_6^{4-}]$ ANIONS. A BUILDING BLOCK APPROACH TO HIGH T_N FERRIMAGNETS

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Abstract. The synthesis and characterization of Prussian blue analogues derived from the pentacyanonitrosylchromate(I) and hexacyanochromate(II) ions are discussed. By addition of triflate salts of either Mn^{II} or Cr^{II}, occasionally in the presence of a cesium source, four new molecular magnets have been obtained: $K_{0.5}Mn[Cr(CN)_5NO]_{0.83}{\bullet}4H_2O{\bullet}1.5MeOH$ (**1**), $Cs_{0.5}Cr[Cr(CN)_5NO]_{0.83}{\bullet}2H_2O{\bullet}0.6MeOH$ (**2**), $Cr[Cr(CN)_5NO]_{0.5}{\bullet}2H_2O{\bullet}1.8MeOH$ (**3**), and $Cr[Cr(CN)_6]_{0.5}{\bullet}3H_2O$ (**4**). The powder XRD patterns for (**1**) and (**4**) can be indexed to face-centered cubic unit cells with a = 10.63(4) and 10.37(4) Å, respectively. IR spectra are consistent with the view that the nitrosyl ligands in the pentacyanonitrosylchromate salts are bridging: the ν_{NO} stretching frequency is ca. 60-110 cm^{-1} higher than that of the potassium salt $K_3[Cr(CN)_5NO]$. The compounds undergo spontaneous ferrimagnetic ordering at temperatures of 31, 89, 127, and 238 K, respectively, and they exhibit hysteretic behavior at 4.5 K with coercive fields of 8, 10, 11, and 330 G. For the solids containing chromium(II) centers, saturation magnetization and room temperature susceptibility measurements suggest that these centers are low-spin (S=1). Overall, the $[Cr(CN)_5NO^{3-}]$ anion affords Prussian blue analogues with lower magnetic ordering temperatures than does the related $[Cr(CN)_6^{3-}]$ anion; this probably reflects the lower symmetry of the pentacyanonitrosylchromate ion and the fact that it contains fewer unpaired electrons.

1. INTRODUCTION.

Of all the classes of molecular magnets,[1,2] Prussian blue analogues constructed from early transition metal hexacyanometalate building blocks such as [$V(CN)_6^{4-}$] and [$Cr(CN)_6^{3-}$] exhibit some of the highest magnetic ordering temperatures. The ability of these solids to retain their magnetism at high temperatures can be ascribed to the three-dimensional nature of the Prussian blue lattice, and to the significant delocalization of spin density onto the cyanide ligands. For example, we recently described the first vanadium-based Prussian blue analogues, $Cs_2Mn^{II}[V(CN)_6]$ and $[Et_4N]_{0.4}Mn[V(CN)_5O_{0.5}]_{0.8}\bullet 1.2H_2O$, which have magnetic ordering temperatures of 125 and 230 K respectively,[3] and Verdaguer has reported a vanadium-containing cyanometalate with the remarkable ordering temperature of 315 K.[4]

As part of an effort to develop new classes of molecular magnets, we have begun an investigation of a new kind of building block: the pentacyanonitrosylmetalate ions [$M(CN)_5NO^{n-}$]. In fact, a few Prussian blue analogues are known that are constructed from pentacyanonitrosylmetalate ions. Cotton briefly described the manganese-based compound $Mn^{II}_3[Mn^I(CN)_5NO]_2$,[5] and several authors have reported the preparation of nitroprusside-based compounds having the general formula $M[Fe^{II}(CN)_5NO]_m\bullet xH_2O$ (M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}).[6-10] The single-crystal structures of several of these solids have been determined.[11-15] Unfortunately, no variable temperature magnetic studies of these compounds were described; furthermore, ferrimagnetic ordering is likely to occur only at very low temperatures (< 5 K) owing to the presence of the diamagnetic Mn^I and Fe^{II} centers in these solids.

Fortunately, paramagnetic examples of pentacyanonitrosylmetalate complexes are known. One of these, the chromium species [$Cr(CN)_5NO^{3-}$], is relatively easy to prepare, is reasonably easy to handle, and carries one unpaired electron in a d_{xy} orbital. By treatment of this anion with suitable paramagnetic cations, new molecular magnets based on the Prussian blue structure should be obtainable. Comparisons of such materials with those derived from the related anion [$Cr(CN)_6^{3-}$] should be of interest. One unanswered question is whether the nitrosyl ligand can form a linear bridge of the sort M-N≡O-M' to another metal cation.

Molecular orbital calculations show that the nitrosyl ligand is a very strong π-acceptor;[16] consequently, there should be extensive delocalization of spin density onto the nitrosyl ligand and magnetic exchange couplings with an adjacent metal center could be enhanced if M-N≡O-M' bridges can be formed. Anions of the type

$[M(CN)_5NO^{n-}]$ are known to have metal-to-ligand charge transfer transitions in their optical spectra, and the excited states are quite long-lived.[17,18] Accordingly, we are especially interested in using these anions as building blocks to synthesize magnets whose magnetic properties would change upon exposure to light.[19]

We will now describe the synthesis, magnetic properties, and solid state structures of new Prussian blue analogues made from the $[Cr(CN)_5NO^{3-}]$ anion; we will also describe our magnetic studies of a Prussian blue analogue "$Cr(CN)_2 \cdot 2H_2O$" based entirely on chromium(II) building blocks.

2. NEW PRUSSIAN BLUE ANALOGUES CONSTRUCTED FROM $[Cr(CN)_5NO^{3-}]$

In 1959, Wilkinson described the preparation of the salt $K_3[Cr^I(CN)_5NO]$ by treatment of CrO_3 with a boiling aqueous solution of KOH, $H_2NOH \cdot HCl$, and KCN.[20] The nitrosyl group is linear as shown by a crystal structure.[21] Since linear nitrosyl groups are assigned a charge of +1, the compound is formally a salt of chromium(I); there is one unpaired electron as shown by its magnetic moment at room temperature.[20] As judged from the frequencies of the ν_{CN} stretching modes, delocalization of spin density onto the cyanide ligands in $[Cr(CN)_5NO^{3-}]$ is very similar to that observed for the $[Cr(CN)_6{}^{3-}]$ anion: the ν_{CN} frequencies are 2120 and 2128 cm^{-1}, respectively.

We find that addition of trifluoromethanesulfonate salts of transition metal cations to the $[Cr(CN)_5NO^{3-}]$ anion affords solids having the general stoichiometry $A_nM[M'(CN)_5NO]_m \cdot$solvate where A is an alkali metal cation. A useful preparative method involves slow diffusion of methanolic solutions of $M(OSO_2CF_3)_2$ into aqueous $K_3[Cr(CN)_5NO]$ at 25 °C. Substitution of cesium for potassium can be achieved by carrying out the procedures in the presence of excess cesium triflate. The solids we have isolated are: yellow $K_{0.5}Mn[Cr(CN)_5NO]_{0.83} \cdot 4H_2O \cdot 1.5MeOH$ (**1**), dark green $Cs_{0.5}Cr[Cr(CN)_5NO]_{0.83} \cdot 2H_2O \cdot 0.6MeOH$ (**2**), and tan $Cr[Cr(CN)_5NO]_{0.5} \cdot 2H_2O \cdot 1.8MeOH$ (**3**). The powder X-ray pattern for (**1**) can be indexed to face-centered cubic structure with a = 10.63(4) Å (Figure 1). If the solid adopts an ordered structure, then the Cr^I ($S = {}^1/_2$) and Mn^{II} ($S = {}^5/_2$) centers occupy alternate lattice positions with vacancies in the former sites. Ayers and Waggoner previously reported that the solids of stoichiometry $A_nM[Fe^{II}(CN)_5NO]_m \cdot xH_2O$, where M is Co^{II} and Ni^{II}, are isomorphous with Prussian blue: they crystallize in

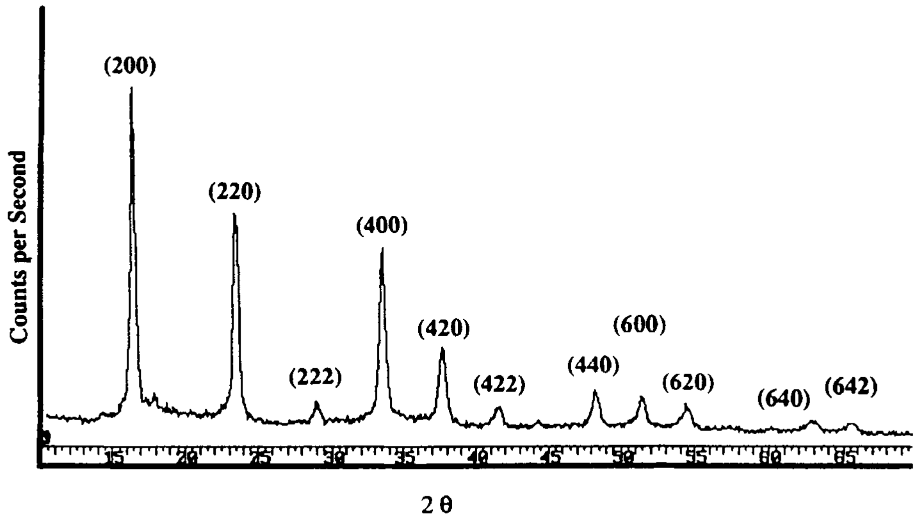

FIGURE 1. Powder X-ray diffraction pattern for (1).

face-centered cubic lattices with lattice constants of approximately 10.25 Å.[7-10] Mullica et al. confirmed this finding; a single crystal analysis of the cobalt compound was refined in the space group $Fm\bar{3}m$ with a = 10.281(2) Å.[12]

The infrared spectrum of (**1**) exhibits sharp and intense absorptions at 2144 and 1694 cm^{-1} for the cyanide and nitrosyl groups, respectively. The infrared spectra of (**2**) (ν_{CN} = 2150 (s), 2057 (m) cm^{-1}; ν_{NO} = 1729 (s) cm^{-1}) and (**3**) (ν_{CN} = 2159 (vs), 2058 (w) cm^{-1}; ν_{NO} = 1741 (vs) cm^{-1}) each contain single sharp nitrosyl bands and two sharp cyanide bands. The presence of two well-separated cyanide bands for (**2**) and (**3**) suggests that there may be some linkage isomerism in these solids.[22-24]

In all of these compounds, the shifting of the cyanide stretching band from 2120 cm^{-1} in $K_3[Cr(CN)_5NO]$ to 2144 -2159 cm^{-1} in (**1**) - (**3**) is indicative of the formation of M-C≡N-M' bridging units and the consequent depopulation of the CN 5σ orbital.[25] The increase of the ν_{NO} stretching frequency from 1631 cm^{-1} in K_3-$[Cr(CN)_5NO]$ to 1694 - 1741 cm^{-1} in (**1**) - (**3**) can be similarly ascribed to the formation of M-N≡O-M' bridges.[26] In comparison, the ν_{NO} stretching frequencies for several $M[Fe(CN)_5NO]$ species, in which the nitrosyl ligands do not bridge to an adjacent transition metal center, are all near 1945 cm^{-1};[10-14] this value is essentially identical to that of 1940 cm^{-1} reported for the sodium salt $Na_2[Fe(CN)_5NO]$-$\cdot 2H_2O$.[10] The inability of the nitrosyl ligand to form bridges in these systems

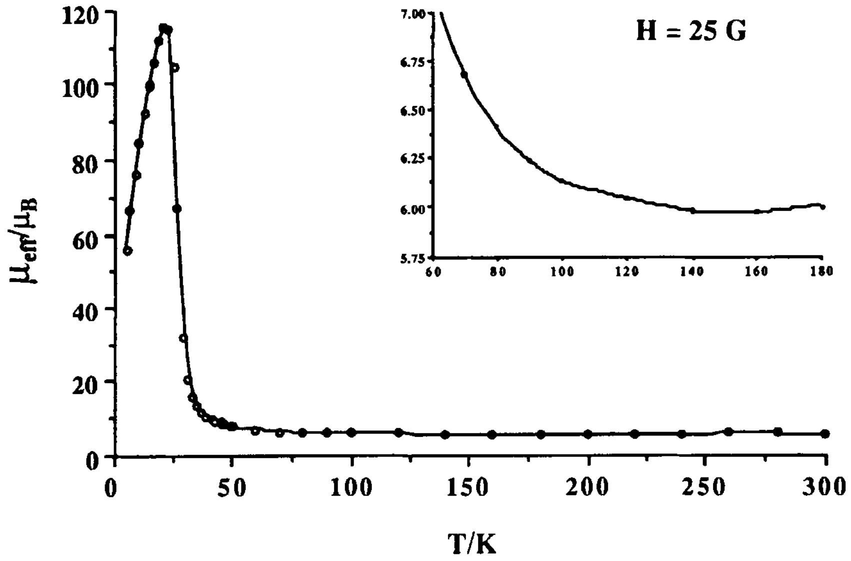

FIGURE 2. Temperature dependence of the magnetic moment per formula unit for (1) in an applied field of 25 Gauss. Inset: expansion of high-temperature region.

presumably is related to the lower partial negative charge on the nitrosyl groups in the dianion [$Fe(CN)_5NO^{2-}$] vs. the trianion [$Cr(CN)_5NO^{3-}$]. Interestingly, no other examples of M-N≡O-M' bridging units have been reported.

Variable temperature magnetic studies of (**1**) - (**3**) have been carried out (Figure 2). For each compound, the magnetic moment per formula unit at 300 K is very close to that calculated from the molecular formula, assuming that the spins are thermally randomized: the values of 6.12, 3.24, and 3.46 μ_B calculated for (**1**) - (**3**) are in close agreement with the experimental values of 6.1, 3.37, and 4.0 μ_B. When the samples are cooled the magnetic moment stays relatively constant until onset of a magnetic ordering transition; below the transition temperature the magnetic moment rapidly increases.

For Prussian blue analogues (and for other magnetic solids constructed from two interpenetrating sublattices), the sign of the local exchange interactions can usually be determined from the shape of the μ_{eff} vs. T curve: for ferrimagnetic

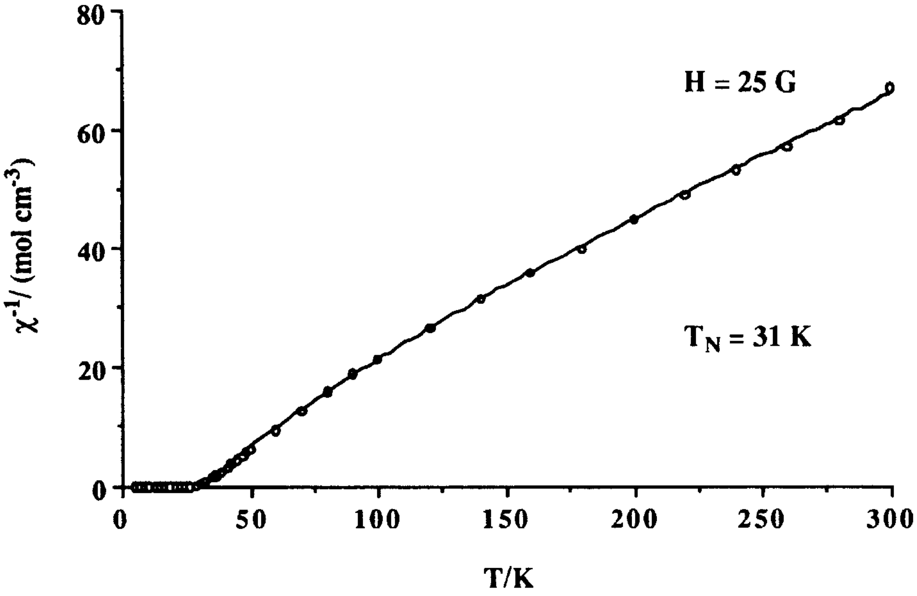

FIGURE 3. Plot of $1/\chi$ vs. T for (1); the fit to Néel's hyperbolic equation is shown.

solids there is a minimum in μ_{eff} above the ordering temperature owing to the effect of short-range antiferromagnetic correlations that cancel spins.[27] Such a minimum is observed for (**1**) - (**3**) and thus all three solids are clearly ferrimagnets; the minimum for (**1**) is very shallow and occurs at ca. 150 K (inset of Figure 2).

Estimates of the magnetic ordering temperatures for (**1**) - (**3**) can be obtained from plots of $1/\chi$ vs. T. The plots are essentially linear in the high temperature region, but deviate hyperbolically at low temperature. The shape of the curve can be fit to Néel's equation $1/\chi = (T - \theta)/C - \xi/(T - \theta')$,[28] where θ and C are the Weiss and Curie constants. The values of θ and C deduced from the fits are given in Table 1. For all three compounds 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: for compounds (**1**) - (**3**) the derived values are 31, 89, and 127 K, respectively (Table 1). Figure 3 shows the data for (**1**).

TABLE 1. Magnetic Data for the New Molecular Magnets.

cmpd	T_N/K	C^a	θ/K	M_{sat}^b
$K_{0.5}Mn[Cr(CN)_5NO]_{0.83}\cdot 4H_2O\cdot 1.5MeOH$ (1)	31	5.42	-105	26.0
$Cs_{0.5}Cr[Cr(CN)_5NO]_{0.83}\cdot 2H_2O\cdot 0.6MeOH$ (2)	89	3.75	-775	7.3
$Cr[Cr(CN)_5NO]_{0.5}\cdot 2H_2O\cdot 1.8MeOH$ (3)	127	4.08	-439	4.7
$Cr[Cr(CN)_6]_{0.5}\cdot 3H_2O$ (4)	238	2.32	-181	4.2

^{a} cm^3 K mol^{-1}. ^{b} kG cm^3 mol^{-1}.

Confirmation of the ferrimagnetic nature of these solids has been obtained from saturation magnetization measurements. The values of the saturation magnetizations (Table 1) are in close agreement with the values predicted from the molecular formulae, assuming isotropic Landé factors, and are considerably smaller than the values expected for ferromagnetic solids.

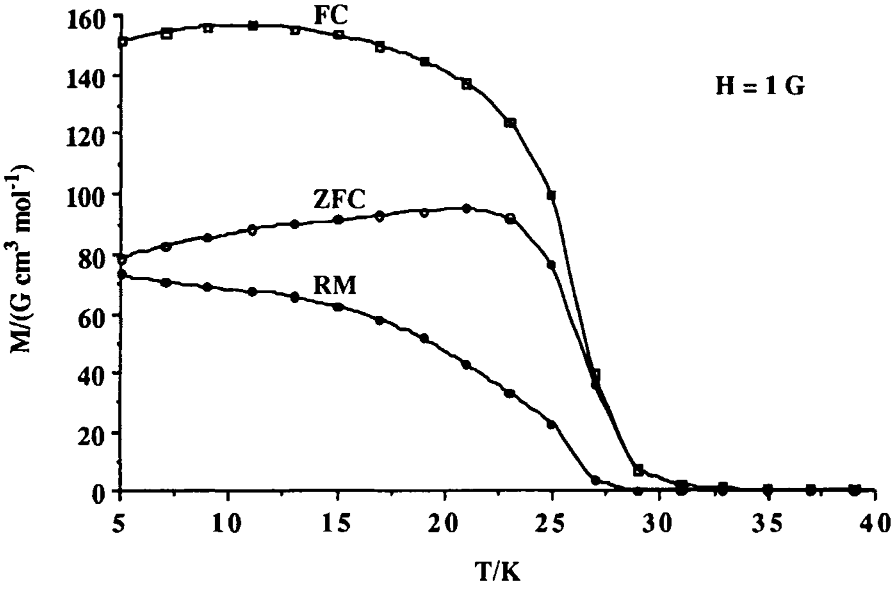

FIGURE 4. Magnetization of (1) as a function of temperature in an applied field of 1 Gauss: ZFC = zero-field-cooled magnetization; FC = field-cooled magnetization; RM = remnant magnetization.

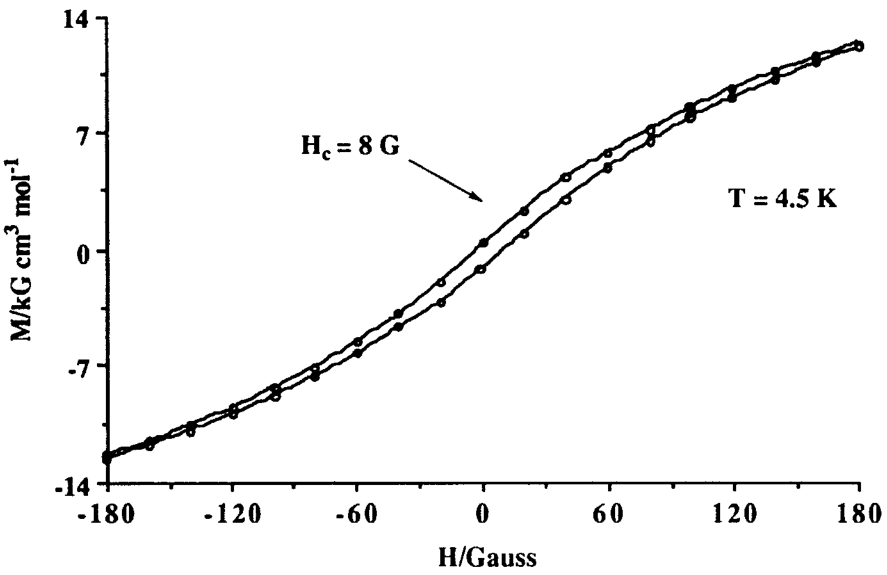

FIGURE 5. Hysteresis for (1) at 4.5 K.

The temperature dependence of the field-cooled, zero-field cooled, and remnant magnetizations for (**1**) clearly shows the onset of long-range magnetic order at 31 K (Figure 4). The remnant magnetization goes to zero at 31 K, and this measurement of the magnetic ordering temperature agrees with that deduced from the Néel hyperbola.

Each of these compounds exhibit hysteresis below the magnetic ordering temperature. The hysteresis loop at 4.5 K for (**1**) is given in Figure 5. The coercive fields for (**1**) - (**3**) are 8, 10, and 11 Gauss, respectively, and the remnant magnetizations are given in Table 2. The coercive fields of (**1**) - (**3**) are relatively small.

Overall, it appears that the [$Cr(CN)_5NO^{3-}$] building block is a useful one for the construction of new molecular magnets. Comparisons with similar magnets prepared from the [$Cr(CN)_6^{3-}$] anion suggest that the magnetic ordering temperatures are generally somewhat higher for the latter. If this is a general phenomenon, then the difference may reflect the lower symmetry of the [$Cr(CN)_5NO^{3-}$] unit and the

TABLE 2. Remnant Magnetizations and Coercive Fields for the New Molecular Magnets at 4.5 K.

cmpd	M_r/G cm^3 mol^{-1}	H_c/G
$K_{0.5}Mn[Cr(CN)_5NO]_{0.83} \cdot 4H_2O \cdot 1.5MeOH$ (1)	800	8
$Cs_{0.5}Cr[Cr(CN)_5NO]_{0.83} \cdot 2H_2O \cdot 0.6MeOH$ (2)	623	10
$Cr[Cr(CN)_5NO]_{0.5} \cdot 2H_2O \cdot 1.8MeOH$ (3)	208	11
$Cr[Cr(CN)_6]_{0.5} \cdot 3H_2O$ (4)	1135	330

consequent local anisotropies generated by the fact that the exchange coupling to the nearest neighbors will depend on whether the linking group is cyanide or nitrosyl. Alternatively, the lower ordering temperatures could simply reflect the fact that $[Cr(CN)_5NO^{3-}]$ has one unpaired electron whereas $[Cr(CN)_6{}^{3-}]$ has three; solids based on the former building block will therefore have fewer exchange coupling pathways.

3. NEW PRUSSIAN BLUE ANALOGUES CONSTRUCTED FROM $[Cr(CN)_6{}^{4-}]$

In 1981, Eaton and Nicholls reported that the slow addition of aqueous chromium(II) with KCN initially affords a deep red solution of the $[Cr(CN)_6{}^{4-}]$ ion, but that continued addition of chromium(II) leads to the precipitation of a dark green solid of stoichiometry $Cr(CN)_2 \cdot 2H_2O$.[29] The IR spectrum (ν_{CN} = 2182, 2062 cm^{-1}), room temperature magnetic moment (2.73 μ_B), and electronic spectrum of the compound were reported. If this solid is a Prussian blue analogue, then it is probably better formulated as $Cr[Cr(CN)_6]_{0.5} \cdot 3H_2O$; this formula explicitly recognizes the likely presence of two types of chromium centers: those in C_6 environments and those in N_xO_{6-x} environments.[30] Owing to the difference in populations in the two sites, the spins will be uncompensated and thus the solid should be a ferrimagnet; furthermore, as judged from our understanding of the exchange mechanism in Prussian blue analogues, the magnetic ordering temperature should be high.[3] Although chromium-based Prussian blue analogues have been described, all contain chromium(III) centers or mixtures of chromium(II) and chromium(III).[4,19,31] The present compound consists only of chromium(II) sites.

We repeated the preparation as described by Eaton and Nicholls, except that we centrifuged off the precipitate under argon and dried it at room temperature under vacuum. The IR band previously reported at 2182 cm^{-1} is evidently due to a chromium(III) impurity; carefully prepared samples have only a weak band at this location vs. a very strong band at 2069 cm^{-1}. In addition, our samples contain about 4 % by weight of potassium.

The XRD patttern of the material can be indexed to a face-centered cubic cell with a = 10.37(4) Å. We find that this material is a molecular magnet: the magnetic moment increases rapidly when the sample is cooled and the Néel hyperbola shows that the magnetic ordering temperature is 238 K (Figure 6). The saturation magnetization indicates that all of the chromium(II) centers are low-spin (Table 2). At 4.5 K, the compound shows hysteresis with H_c = 330 G.

Thus this all-chromium(II) compound has a magnetic ordering temperature that is similar those of other chromium-containing Prussian blue analogues[4] and that rivals the highest ordering temperatures seen for any molecular magnet. We are currently investigating the use of the $[Cr(CN)_6{}^{4-}]$ anion to prepare other solids with the Prussian blue structure.

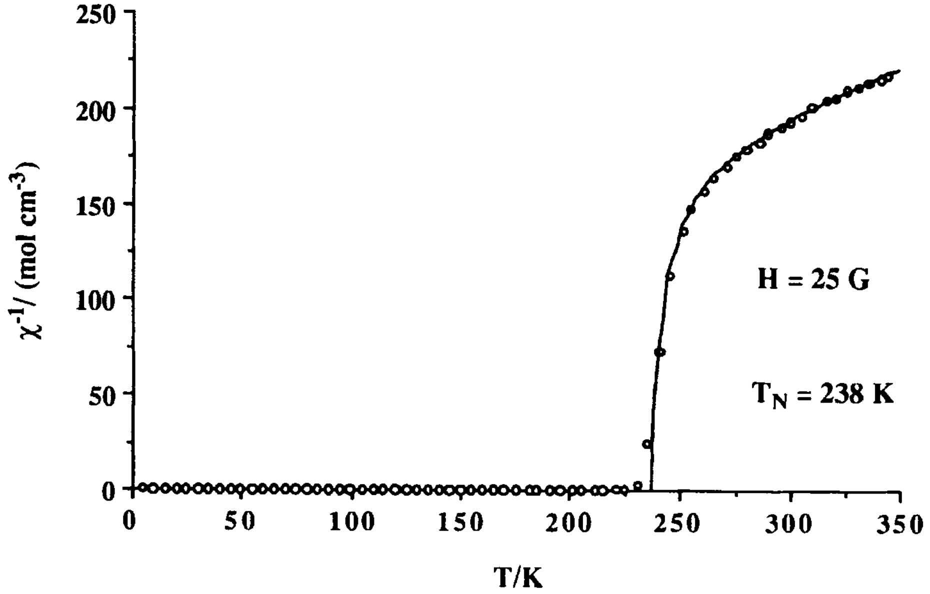

FIGURE 6. Plot of 1/χ vs. T for (4); the fit to Néel's hyperbolic equation is shown.

ACKNOWLEDGMENTS

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