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Synthesis, characterization, and magnetic properties of tetracyanonitridochromates

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Abstract

The reaction of $S = 1/2$ $[\text{PPh}_4]_2[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4]$ with $[\text{M}(\text{NCMe})_x][\text{BF}_4]_2$ ($\text{M} = \text{V}, \text{Fe}, \text{Co}, \text{Ni}$, $x = 6$; $\text{M} = \text{Mn}$, $x = 4$) and $[\text{Cr}^{\text{II}}(\text{NCMe})_6](\text{BARF})_2$ [$\text{BARF} = \text{tetrakis}(3,5\text{-trifluoromethylphenyl})\text{borate}$] led to materials of nominal $\text{M}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4] \cdot \text{MeCN}$ composition, albeit contaminated with cationic and/or anionic impurities. $\text{V}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4]$ exhibits strong antiferromagnetic coupling ($\theta = -352$ K) and orders as an antiferromagnet ($T_c = 10.0$ K) while $\text{M}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4]$ ($\text{M} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) are weak ferromagnets (canted antiferromagnets) that order between 4.5 (Co) and 10.5 (Fe) K.

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1. Introduction

Several materials belonging to the growing Prussian blue, $\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$, family, $\text{M}^{\text{I}}[\text{M}(\text{CN})_6]_x$, of molecule-based magnets order above room temperature [1]. Accordingly, Prussian blue compounds have been structurally [2], spectroscopically [3], and magnetically [1,4] studied in detail. Efforts to modify the basic coordination sphere of the building block have involved adding or removing cyano ligands (e.g. $[\text{M}(\text{CN})_8]^{3-}$ [5a], $[\text{Mo}(\text{CN})_7]^{4-}$ [5e], and $[\text{M}^{\text{II}}(\text{CN})_4]^{2-}$ [5b–5d]) and substitution of one cyano group with a nitrosyl ligand [6]. In 1998, a spectroscopic study of nitrido complexes, of $[\text{M}^{\text{V}}(\text{N})(\text{CN})_x]^{2-x}$ ($\text{M} = \text{Cr}, \text{Mn}$; $x = 4, 5$) composition, outside of the context of molecule-based magnetism, led to potential building blocks for another branch of the Prussian blue family [7]. The $S = 1/2$ $[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_5]^{3-}$ and $[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4]^{2-}$ building blocks contain a nitrido ligand that could potentially bind a second metal via a one atom bridge with the expectation of increased magnetic exchange with respect to the

$[\text{Cr}^{\text{III}}(\text{CN})_6]^{3-}$ derivatives. Herein, we report molecule-based magnets possessing the tetracyanonitridochromate(V) building block with the general formula $\text{M}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4] \cdot \text{MeCN}$. The $[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_5]^{3-}$ building block is soluble in highly polar media, where the cyanide *trans* to the nitrido ligand is labile, and tetracyanonitrido products are isolated even in the presence of excess cyanide. Hence, materials of $\text{M}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_5]$ composition have been elusive and could not be studied.

2. Experimental

2.1. Synthesis

All preparations were carried out under an inert atmosphere with minimal exposure to light. Acetonitrile was twice distilled (CaH_2 , P_2O_5) under nitrogen. $[\text{PPh}_4]_2[\text{Cr}(\text{N})(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ [7], $[\text{M}(\text{NCMe})_x][\text{BF}_4]_2$ ($\text{M} = \text{V}, \text{Fe}, \text{Co}, \text{Ni}$, $x = 6$; $\text{M} = \text{Mn}$, $x = 4$) and $[\text{Cr}^{\text{II}}(\text{NCMe})_6](\text{BARF})_2$ [8] [$\text{BARF} = \text{tetrakis}(3,5\text{-trifluoromethylphenyl})\text{borate}$] were prepared according to literature methods. Ubiquitous water was removed from $[\text{M}^{\text{II}}(\text{NCMe})_x](\text{BF}_4)_2$ prior to use by stirring an

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acetonitrile solution over activated molecular sieves, filtering, and removing the solvent.

$\text{Ni}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4] \cdot \text{MeCN}$ was prepared from a 1:1 mixture of $[\text{Ni}^{\text{II}}(\text{NCMe})_6][\text{BF}_4]_2$ (95.6 mg, 0.200 mmol) and $[\text{PPh}_4]_2[\text{Cr}(\text{N})(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ (259.2 mg, 0.2932 mmol). An acetonitrile solution (25 ml) of $[\text{PPh}_4]_2[\text{Cr}(\text{N})(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ was slowly added dropwise to an acetonitrile solution (25 ml) of the metal salt with vigorous stirring. The immediate precipitate that formed was subjected to three cycles of centrifugation and washing with acetonitrile. After the final washing, the supernatant was removed and the solid was dried in vacuo. Yield: 90% (Found for $\text{Ni}[\text{Cr}(\text{N})(\text{CN})_4] \cdot 0.52\text{Me} \cdot 0.3\text{H}_2\text{O} \cdot 0.14[\text{Ni}(\text{NC-Me})_6](\text{BF}_4)_2$: C, 25.02; H, 1.40; N, 27.66. Anal. Calc. [9]: C, 25.02; H, 1.46; N, 27.62%).

$\text{Co}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4] \cdot \text{MeCN}$ (Yield: 34%), $\text{Fe}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4] \cdot \text{MeCN}$ (Yield: 64%), [Found for $\text{Fe}[\text{Cr}(\text{N})(\text{CN})_4] \cdot \text{MeCN} \cdot \text{H}_2\text{O} \cdot 0.11[\text{Fe}(\text{NCMe})_6](\text{BF}_4)_2$: C, 26.05; H, 2.14; N, 27.72. Anal. Calc.: C, 26.06; H, 2.09; N, 27.65%], $\text{Mn}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4] \cdot \text{MeCN}$ (Yield: 37%), $\text{Cr}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4] \cdot \text{MeCN}$ (Yield: 55%), and $\text{V}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4] \cdot \text{MeCN}$ (Yield: 82%) were prepared as described above.

2.2. Spectroscopic measurements

Infrared spectra were recorded on a Bio-Rad FTS-40 FTIR spectrometer as KBr pellets in the 400–4000 cm^{-1} region.

2.3. Magnetic measurements

Magnetic susceptibility measurements were carried out on powdered samples in airtight holders in the temperature range 2–300 K as previously described [10]. Low field measurements were obtained using a shielded Quantum Design MPMS-5XL SQUID a.c./d.c. magnetometer that had been degaussed and reset. A.c. susceptibility (10, 100, and 1000 Hz) data were collected in a 1 Oe a.c. field. High field (>5 T) measurements were carried out on a Quantum Design PPMS magnetometer. The diamagnetic contribution of the sample holder was independently determined and was added to the diamagnetic contribution of the sample calculated from Pascal's constants.

3. Results and discussion

The reaction of $[\text{PPh}_4]_2[\text{Cr}(\text{N})(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ [7] with $[\text{M}(\text{NCMe})_x][\text{BF}_4]_2$ ($\text{M} = \text{V}, \text{Fe}, \text{Co}, \text{Ni}$, $x = 6$; $\text{M} = \text{Mn}$, $x = 4$) and $[\text{Cr}(\text{NCMe})_6](\text{BARF})_2$ [8] leads to a new family of molecule-based magnets possessing $\text{M}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4]$ ($\text{M}^{\text{II}} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) stoichiometry. The elemental analysis and infrared spectra show traces of inclusion impurities and systema-

tic studies did not reveal ideal conditions for the exclusion of starting material. $[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4]^{2-}$ has one unpaired electron localized in the Cr^{V} d_{xy} orbital, which enables a prediction of the magnetic properties of the materials based on whether the M^{II} possesses unpaired electron spins in orbitals that are orthogonal or non-orthogonal to the Cr^{V} d_{xy} orbital [7].

3.1. Infrared spectroscopy

The cyano and nitrido stretching regions of the infrared spectra of the tetracyanonitridochromates are shown in Fig. 1. Peaks consistent with the presence of bound acetonitrile were observed at 3000 and 2937 (ν_{CH}); 2304 and 2283 ($\nu_{\text{C}=\text{N}}$); and 1439, 1410, and 1369 (δ_{CH}) cm^{-1} . The $\text{C} \equiv \text{N}$ stretching related to $[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4]^{2-}$ occurs between 2100 and 2170 cm^{-1} for all of the compounds. $\text{M}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4]$ ($\text{M} = \text{Fe}, \text{Cr}$) show distinct splitting of the cyano absorption attributed to mixed oxidation states and ligand isomerization. The high energy ($\nu_{\text{C}=\text{N}}$) band, resulting from $\text{Cr}^{\text{V}}-\text{C} \equiv \text{N}-\text{M}^{\text{II}}$ bonding, was blue shifted ~ 20 to 40 cm^{-1} relative to $[\text{PPh}_4]_2[\text{Cr}(\text{N})(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ (2131 cm^{-1}). The $\text{Cr} \equiv \text{N}$ stretching mode, which appears at 1046 cm^{-1} in $[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4]^{2-}$, is red shifted and split and occurs at 1031, 1007 and 950–928 cm^{-1} for $\text{M}^{\text{II}} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$. Shifting of ($\nu_{\text{Cr}=\text{N}}$) to higher energy is normally observed upon coordination of a Lewis acid [11]. However, competition between Cr^{V} and M^{II} for back-bonding with the cyanide π^* orbitals leads to increased electron density in the Cr^{V} d-orbitals, which are thus able to accept less electron density from the nitrido ligand resulting in a weaker $\text{Cr}^{\text{V}} \equiv \text{N}$ bond. This is also observed for $[(\text{CN})_5\text{Mn}^{\text{V}}\text{NMn}^{\text{II}}(\text{CN})_5]^{6-}$ [12]. Also,

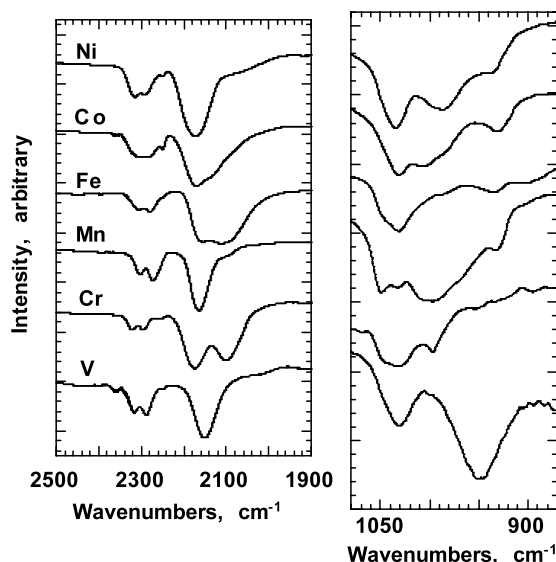


Fig. 1. Infrared spectra of the tetracyanonitridochromates.

Table 1
Summary of the IR $\nu_{\text{C=N}}$ and $\nu_{\text{Cr=N-M}}$ data for $\text{M}[\text{Cr}(\text{N})(\text{CN})_4] \cdot x\text{MeCN}$

M	$\nu_{\text{C=N}}$ (cm^{-1})	$\nu_{\text{Cr=N-M}}$ (cm^{-1})	ν_{MC} (cm^{-1})
[PPh ₄] ₂	2131	1046	
V	2151	1031, 947	498
Cr	2175, 2100	1032, 997	511
Mn	2165	1032, 1008, 995, 932	500
Fe	2154, 2111	1032, 935, 900	508
Co	2170, 2132	1031, 1006, 931	497
Ni	2173	1035, 986, 935	506

a M–C bending mode is observed at $\sim 503 \text{ cm}^{-1}$ (Table 1).

3.2. Magnetic properties

Spectroscopic studies of $[\text{PPh}_4]_2[\text{Cr}(\text{N})(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ revealed that the unpaired electron of Cr^{V} is localized in the d_{xy} orbital, as expected for an axially compressed C_{4v} complex [7]. Hence, ferromagnetic coupling is expected for $\text{M}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4]$ when M^{II} has unpaired electrons in orbitals that are orthogonal to the Cr^{V} d_{xy} orbital, e.g., for Ni^{II} , and antiferromagnetic coupling that can lead to ordering as a ferrimagnet is expected when M^{II} has unpaired electrons in non-orthogonal orbitals. Due to the aforementioned inclusion impurities, which vary among and between samples, the quantitative values of χT are problematic and are reported as guides and relative trends, e.g. as $\chi^{-1}(T)$ or $\chi T(T)$ plots. Magnetic ordering is attributed to the targeted compounds, namely $\text{M}[\text{Cr}(\text{N})(\text{CN})_4]$ ($\text{M} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$).

The magnetic susceptibilities, χ , of $\text{M}[\text{Cr}(\text{N})(\text{CN})_4]$ ($\text{M}^{\text{II}} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) were determined between 2 and 300 K and representative $\chi^{-1}(T)$, and $\chi T(T)$ for $\text{M} = \text{V}, \text{Mn}, \text{Cr}, \text{Fe}, \text{Ni}$ are presented in Fig. 2. The values of χT at room temperature are 0.98 ($S = 3/2 \text{ V}^{\text{II}}$, 2.250), 1.19 ($\text{Cr}^{\text{II/III}}$), 3.53 ($S = 5/2 \text{ Mn}^{\text{II}}$, 4.750), 2.72 (Fe^{II}), 2.00 ($S = 3/2 \text{ Co}^{\text{II}}$, 2.250), and 1.30 emu K mol^{-1} ($S = 1 \text{ Ni}^{\text{II}}$, 1.375 emu K mol^{-1} expected). These values are low due to difficulty in producing the fast forming insoluble precipitates without starting material inclusion impurities. In all cases, the $\chi^{-1}(T)$ data is linear at high temperature and can be fit to the Curie–Weiss expression, $\chi \propto (T - \theta)^{-1}$, $\theta = -352$ (V^{II}), -99 (Cr^{II}), -19 (Mn^{II}), -7 (Fe^{II}), -14 (Co^{II}), and $+32$ K (Ni^{II}). The negative θ values observed for $\text{M}^{\text{II}} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}$, and Co , indicate dominant antiferromagnetic coupling, while $\theta > 0$ for $\text{M} = \text{Ni}$ indicates dominant ferromagnetic coupling. Furthermore, for $\text{M}^{\text{II}} = \text{Cr}, \text{Mn}, \text{Fe}$, and Co a second linear region at lower temperature designated as θ' [10,13] with values of $+38$ (Cr^{II}), $+18$ (Mn^{II}), $+10$ (Fe^{II}), and $+1$ K (Co^{II}) is consistent with shorter-range interactions and ferrimagnetic behavior.

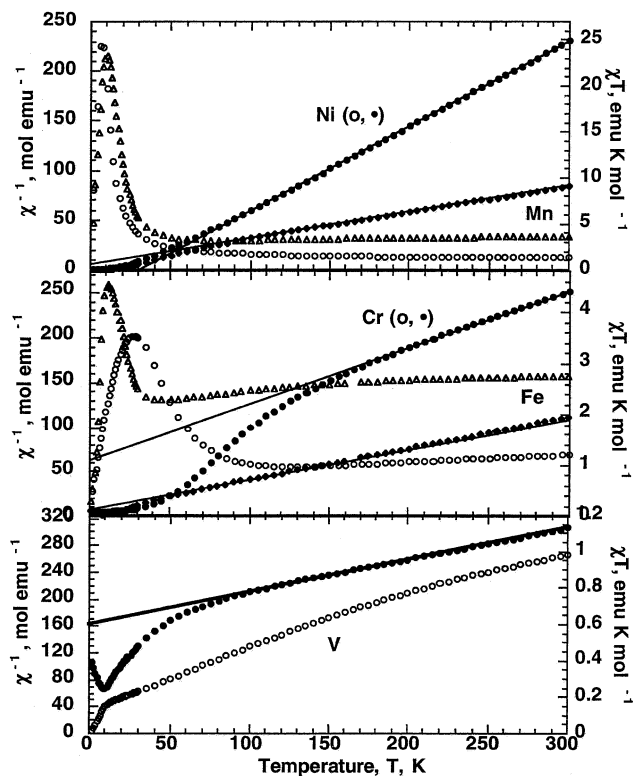


Fig. 2. Temperature dependence of the reciprocal molar magnetic susceptibility, χ^{-1} , (solid symbols) and χT (open symbols) of $\text{M}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4]$ [$\text{M} = \text{Ni}$ (\circ), Mn (Δ)] (top), [$\text{M} = \text{Cr}$ (\circ), Fe (Δ)] (middle), and ($\text{M} = \text{V}$) (bottom). Solid line is a visual guides for θ (-99 K, Cr), (-7 K, Fe), ($+32$ K, Ni), (-19 K, Mn), (-352 K, V).

$\text{Ni}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4] \cdot \text{MeCN}$ is the only $\text{M}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4]$ that solely exhibits ferromagnetic coupling, due to occupation of the Ni^{II} e_g orbitals with unpaired electrons that are orthogonal to the unpaired electron in the Cr^{V} d_{xy} orbital.

The very strong antiferromagnetic coupling, -352 K, of $\text{V}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4] \cdot \text{MeCN}$ accounts for the suppression of the observed room temperature χT value relative to that expected for an uncoupled $S = 3/2 + 1/2$ spin system to 1.035 emu K mol^{-1} in good agreement with the observed value of 0.98 emu K mol^{-1} .

$\text{M}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4]$ ($\text{M} = \text{Fe}, \text{Cr}$) exhibit complex behavior ascribed to partial electron transfer and/or ligand isomerization; behavior similar to that reported for $[\text{Fe}[\text{Mn}(\text{CN})_6]^-]$ [14]. The expected room temperature χT value for a compound containing 50% high spin Fe^{II} ($S = 2$), 50% low spin Fe^{III} ($S = 1/2$), 50% Cr^{V} ($S = 1/2$), and 50% Cr^{IV} ($S = 0$) is 1.83 emu K mol^{-1} while the expectation for a compound containing 50% high spin Fe^{II} ($S = 2$), 50% low spin Fe^{II} ($S = 1$) [15], 100% Cr^{V} ($S = 1/2$) is 2.32 emu K mol^{-1} . The low spin Fe^{II} expectation is similar to the experimentally determined value of 2.02 emu K mol^{-1} . In $\text{Cr}[\text{Cr}(\text{N})(\text{CN})_4] \cdot \text{MeCN}$, $\text{Cr}^{\text{II}}:\text{Cr}^{\text{III}}$ and $\text{Cr}^{\text{V}}:\text{Cr}^{\text{IV}}$ are in a 90:10 ratio as determined from integrating the area under the cyano stretch

of the infrared spectrum [16]. The expected room temperature χT value for a system containing 90% Cr^{II} ($S=1$)/ Cr^{V} ($S=1/2$) and 10% Cr^{III} ($S=3/2$)/ Cr^{IV} ($S=1/2$) is $1.07 \text{ emu K mol}^{-1}$ and is close to the observed value of $1.19 \text{ emu K mol}^{-1}$ assuming $g=2.0$.

A.c. susceptibility studies confirm that $\text{M}[\text{Cr}(\text{N})(\text{CN})_4]$ ($\text{M}^{\text{II}} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) magnetically order with T_c , taken at the maximum in $\chi'(T, 10 \text{ Hz})$, of 10.0 (V), 6.0 (Cr), 7.5 (Mn), 10.5 (Fe), 3.5 (Co), and 4.5 K (Ni) (Fig. 3). The low ordering temperatures of the tetracyanonitridochromates, relative to their

hexacyano counterparts, e.g. $\text{CsNi}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ ($T_c = 90 \text{ K}$) [17], $\text{CsMn}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot \text{H}_2\text{O}$ ($T_c = 90 \text{ K}$) [18], and $\text{Cr}_{1.5}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ ($T_c = 240 \text{ K}$) [19], are attributed to geometrical, charge, and dimensionality differences. The axially compressed pseudo square-pyramidal environment of the nitrido complexes leads to poor orientation and overlap of the metal and ligand orbitals. The orbital overlap is further diminished by contraction of the chromium based d-orbitals upon oxidation from Cr^{III} to Cr^{V} . However, comparison with the two dimensional compounds, $[\text{NiL}^1]_3[\text{Cr}^{\text{III}}(\text{CN})_6]_2 \cdot$

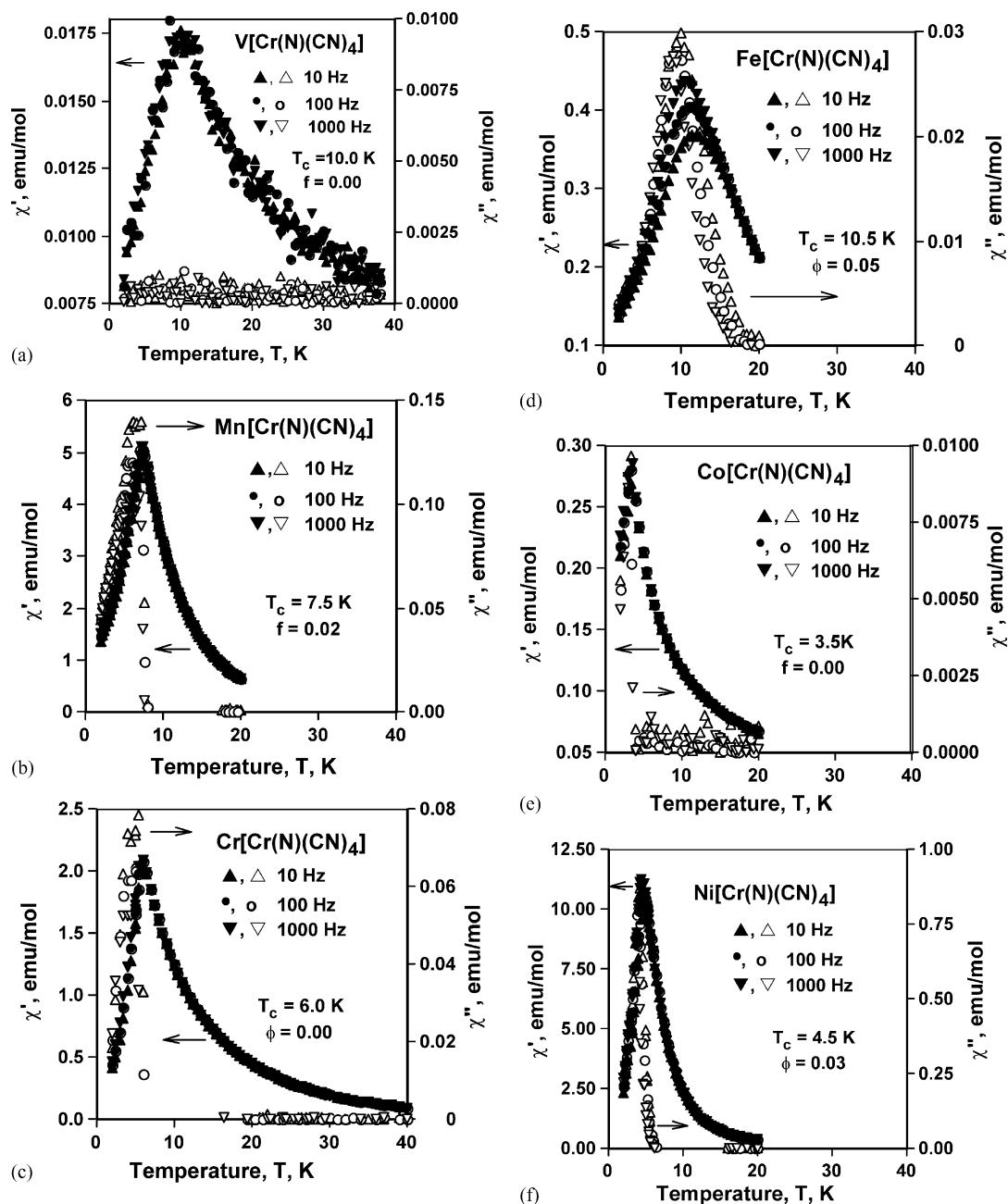


Fig. 3. Temperature dependencies of the in-phase (real), χ' , and out-of-phase (imaginary), χ'' , a.c. susceptibility of $\text{M}^{\text{II}}[\text{Cr}(\text{N})(\text{CN})_4]$ ($\text{M} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co},$ and Ni).

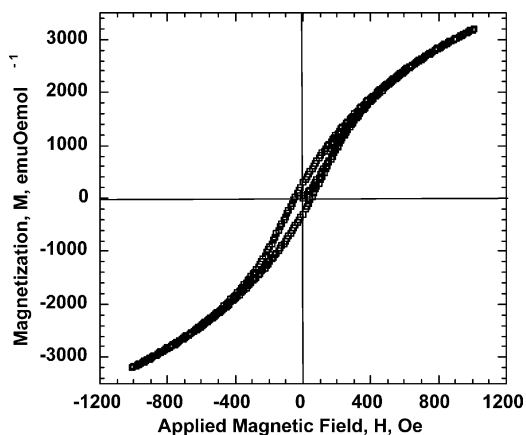


Fig. 4. Hysteresis curve of $\text{Ni}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4]$ at 2 K.

$7\text{H}_2\text{O}$ ($T_{\text{N}} = 13.0$ K), $[\text{NiL}^2]_3[\text{Cr}^{\text{III}}(\text{CN})_6]_2 \cdot 9\text{H}_2\text{O}$ ($T_{\text{N}} = 11.9$ K), and $[\text{NiL}^2]_3[\text{Cr}^{\text{I}}(\text{CN})_5(\text{NO})]_2 \cdot 9\text{H}_2\text{O}$ ($T_{\text{c}} = 4.3$ K) ($L^1 = 3,10$ -dimethyl-1,3,4,5,10,12-hexaazacyclooctadecane; $L^2 = 3,10$ -diethyl-1,3,4,5,8,10,12-hexaazacyclooctadecane) [20], suggests that the factor contributing the most to the ordering temperatures is likely the reduced dimensionality.

The a.c. susceptibility data show peaks in both the in-phase, $\chi'(T)$, and out-of-phase, $\chi''(T)$, components consistent with the formation of ferri- or. $\text{V}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4]$ is an exception as only a peak in $\chi'(T)$ is observed (Fig. 3 top) indicating that it orders as an antiferromagnet at 10.0 K, except for $M = \text{V}$ all members of this family should exhibit hysteretic behavior.

The observed frequency dependence can be parameterized by ϕ [21]

$$\phi = \Delta T_{\text{f}} / [T_{\text{f}} \Delta(\log f)]$$

where T_{f} is the temperature of the peak in the lowest frequency (10 Hz) data, f is the frequency in Hertz, and the greater the frequency dependence the larger the value of ϕ (i.e. the greater the spin glass behavior). $M[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4]$ ($M = \text{V}, \text{Cr}, \text{Co}$) have the lowest values of ϕ , while $\text{Fe}[\text{Cr}(\text{N})(\text{CN})_4]$ shows the largest frequency dependence ($\phi = 0.05$) of the series, and hence is best described as a spin glass. Spin glass behavior

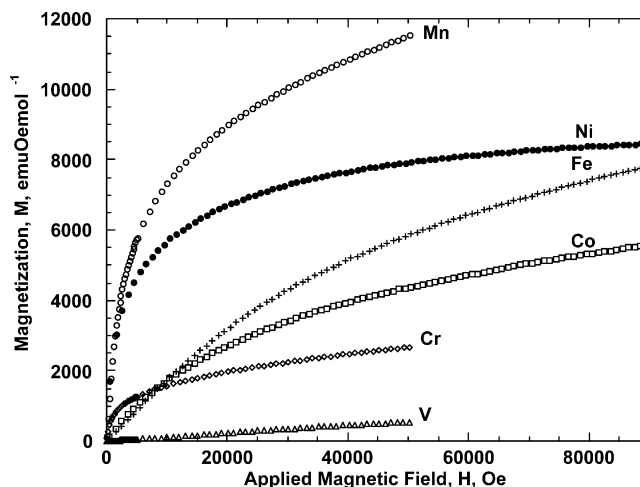


Fig. 5. $M(H)$ for $M^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4]$ ($M^{\text{II}} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$).

results from randomness within a crystal (e.g. site disorder, bond disorder, etc.) and is consistent with multiple spin bearing species and partial ligand isomerization.

Hysteresis is observed for $\text{Ni}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4]$ at 2 K (Fig. 4) with a coercive field of 46 Oe. Measurements conducted on the other members of the study show similar coercive fields (Table 2).

Magnetization versus applied magnetic field, $M(H)$, studies (Fig. 5) reveal that none of these magnetic materials approach saturation at the experimental fields (5 or 9 T). Saturation magnetization of $16755 \text{ emu Oe mol}^{-1}$ is not achieved for ferromagnetic $\text{Ni}^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4]$ at 2 K and 9 T as the value is $8470 \text{ emu Oe mol}^{-1}$ suggesting that it is a weak ferromagnet. Likewise the observed values of 555 (V^{II} , 11,170), 2675 ($\text{Cr}^{\text{II/III}}$, 6875), 11520 (Mn^{II} , 22 340), 7820 (Fe^{II} , 12 846), and 5580 (Co^{II} , 11 170) emu Oe mol^{-1} expected suggest antiferromagnetic coupling for this class of materials. While the experimental values are partially suppressed by impurities the experimental magnetization values at 5 or 9 T are $\sim 50\%$ of the magnitude of the expected saturation magnetization values for ferro- or ferri-magnetically aligned spins indicating canting of the spins relative to the applied magnetic field. The ex-

Table 2

Summary of magnetic data for $M^{\text{II}}[\text{Cr}^{\text{V}}(\text{N})(\text{CN})_4]$

M^{II}	T_{c} (K) ^a	χT_{RT} (emu K mol^{-1})	θ (K)	θ' (K)	M (emu Oe mol^{-1})	ϕ ^b	H_{cr} (Oe)
V	10.0 ^c	0.98	-352		555 (5 T)	0.00	^c
Cr	6.0	1.19	-99	+38	2674 (5 T)	0.00	^c
Mn	7.5	3.53	-19	+18	11 524 (5 T)	0.02	^c
Fe	10.5	2.72	-7	+10	7822 (9 T)	0.05	^c
Co	3.5	2.00	-14	+1	5581 (9 T)	0.00	34
Ni	4.5	1.30	+32		8472 (9 T)	0.03	46

^a Determined from the peak of the 10 Hz a.c. susceptibility data.

^b $\phi = \Delta T_{\text{f}} / [T_{\text{f}} \Delta(\log \omega)]$, T_{f} = peak in 10 Hz data, ω = frequency.

^c Not determined.

tremely low magnetization of 555 emu Oe mol⁻¹ for V^{II}[Cr^V(N)(CN)₄], relative to the expectation of a ferrimagnetically ordered $S = 3/2 - 1/2$ system confirms the a.c. susceptibility data, which show that this compound is an antiferromagnet below 10 K. The residual magnetization may result from defects, as reported for V^{III}[Cr^{III}(CN)₆] [1c]. The mechanism for compensation of the magnetic moment at low temperature is unclear. The magnetic data are summarized in Table 2.

4. Conclusion

M^{II}[Cr^V(N)(CN)₄]·MeCN (M = Cr, Mn, Fe, Co, Ni) order as weak ferromagnets (canted antiferromagnets) while V^{II}[Cr^V(N)(CN)₄]·MeCN is an antiferromagnet. It was possible to predict the type of magnetic ordering that would occur in these compounds based on orbital alignment arguments. However, the distorted geometry of the building block and the highly contracted nature of the Cr^V orbitals, along with decreased dimensionality, led to suppressed ordering temperatures of the tetracyanonitridochromates relative to their [Cr^{III}(CN)₆]³⁻ counterparts. M[Cr(N)(CN)₄]·MeCN (M = Fe, Cr) displayed complex behavior resulting from partial electron transfer and ligand isomerization.

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