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Synthesis and Magnetization of New Room-Temperature Molecule-Based Magnets: Effect of Stoichiometry on Local Magnetic Structure by X-ray Magnetic Circular Dichroism

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Abstract: The synthesis and the magnetic properties of two new bimetallic chromium−vanadium ferrimagnets, compounds **1** and **2**, are reported. They belong to a set of nonstoichiometric Prussian blue analogues $C^{I}_{y}V[Cr^{III}(CN)_6]_z \cdot nH_2O$ (C, alkali cation) with T_C varying between 295 and 315 K ($T_C = 310$ K for **1** and 315 K for **2**). They are obtained through mild chemistry from the molecular precursor $[Cr^{III}(CN)_6]^{3-}$ and from vanadium V^{II} salts. The synthetic conditions determine (i) the oxidation state of the vanadium (V^{II}, V^{III}, or V^{IV}), (ii) the stoichiometry, and (iii) hence the magnetic properties. The reported systems present a larger magnetization than the first reported V−Cr analogue ($0.36N_A\beta$ for **1** and $0.40N_A\beta$ for **2**). Furthermore, X-ray magnetic circular dichroism (XMCD) data demonstrate (i) the short-range antiferromagnetic coupling between the spins borne by the chromium(III) and vanadium ions and (ii) the reversal of the local magnetization on vanadium and chromium when changing the stoichiometry.

Introduction

The rational design of molecule-based magnets with tunable Curie temperature T_C up to room temperature is possible in the Prussian blue family, with general formula $C^{I}_{y}A[B(CN)_6]_z \cdot nH_2O$, where A and B are paramagnetic transition metal ions and C is an alkali cation.[1] The best choice for the A/B pair of transition metal ions to get high Curie temperatures is made possible by the use of a simple orbital model, based on the symmetry and on the energy of the A and B magnetic orbitals.[2,3] The compound which, up to now, presents the highest T_C is obtained through mild chemistry methods by mixing aqueous solutions of hexacyanochromate $[Cr^{III}(CN)_6]^{3-}$ and of a V^{2+}_{aq} Lewis acid. It is a nonstoichiometric system formulated $V^{II}_{0.42}V^{III}_{0.58}[Cr^{III}(CN)_6]_{0.86} \cdot 2.8H_2O$.[4] Changes in the synthetic conditions lead to a set of vanadium−chromium compounds with formula $C^{I}_{y}V[Cr^{III}(CN)_6]_z \cdot nH_2O$. In our hands, these compounds are most often amorphous room-temperature ferrimagnets which present T_C values varying between 295 and 315 K and different magnetization properties.[5]

We undertook the present study to better understand the variation of the magnetic properties with the synthetic conditions, particularly with the stoichiometry and with the oxidation state of the vanadium ions. The oxidation of the initial vanadium(II) into vanadium(III) and vanadium(IV) is expected to have a direct influence on the electronic structure, on the magnitude of exchange interaction and finally on the macroscopic magnetic properties.

In all the cases, the short-range vanadium chromium interaction is foreseen as strongly antiferromagnetic due to the overlap of t_{2g} magnetic orbitals on both ions. The antiparallel alignment of the neighboring spins in the magnetically ordered phase leads to a resulting total magnetization M_T which is the difference between the magnetization arising from the subset of chromium ions M_{Cr} and the one from the subset of vanadium ions, M_V:

$$M_T = |M_{Cr} - M_V|$$

M_T is expected to have small absolute values. Furthermore, two situations may arise; one when the larger magnetic moments are borne by the chromium ions and are aligned parallel to an external applied field ($M_{Cr} > M_V$) and the other when $M_V > M_{Cr}$. In the latter case, the sign of the quantity ($M_{Cr} - M_V$) is reversed and the magnetic moments of vanadium ions now lie parallel to the field. Therefore, the stoichiometry of the compound and the oxidation states of the vanadium ions

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determine not only the absolute value of the overall magnetization M_T but also the local orientation of the spins in the field.

Conventional magnetization measurements give the absolute value of the macroscopic magnetization but not the local magnetization. Instead, X-ray magnetic circular dichroism (XMCD), a new X-ray spectroscopy developed with synchrotron radiation and first observed in 1987,[6] is an element and orbital selective magnetic local probe. We report XMCD results at the K edges of vanadium and chromium in two new room-temperature ferrimagnets, designed to give enhanced magnetization, in which local reversal of the magnetization is expected.

Experimental Section

Synthesis. Compound **1** and compound **2** were synthesized under anaerobic conditions, using the Schlenck's technique.

$V^{II}_{0.45}V^{III}_{0.53}[V^{IV}O]_{0.02}[Cr^{III}(CN)_6]_{0.69}(SO_4)_{0.23}\cdot 3.0H_2O\cdot 0.02K_2SO_4$ (1).[7] Compound **1** was synthesized by mixing of 1:1 aqueous alcoholic solutions (water:ethanol, 1:1) of $K_3[Cr^{III}(CN)_6]$ (0.25 g, 0.75 mmol, 10 mL) and $K_2[V^{II}(H_2O)_6](SO_4)_2$ (0.42 g, 1 mmol, 10 mL). To reduce the oxidation of the vanadium(II) ions, as soon as the precipitate appeared it was filtered off, washed one time with a 1:1 water:ethanol mixture and then dried under vacuum; the contact time between the product and the water was no longer than 5 min. As a consequence, some diamagnetic potassium and sulfate impurities were not totally washed out. The ($V^{IV}O$) moieties represent 2% of the total amount of vanadium and can be neglected in first approximation when interpreting the magnetic properties.

$Cs^{I}_{0.82}V^{II}_{0.66}[V^{IV}O]_{0.34}[Cr^{III}(CN)_6]_{0.92}(SO_4)_{0.203}\cdot 3.6H_2O$ (2).[8] Compound **2** was synthesized by mixing aqueous solutions of $K_3[Cr^{III}(CN)_6]$ (0.25 g, 0.75 mmol, 10 mL) and $Cs^{I}_2[V^{II}(H_2O)_6](SO_4)_2$ (0.61 g, 1 mmol, 10 mL). The precipitate was filtered off, washed five times with water and dried under vacuum. The contact with water was longer than in the case of compound **1** (about 30 min). In these conditions, the sulfate salt was washed out, the oxidation of the vanadium(II) ions became effective, and the amount of vanadyl significant.

Compounds **1** and **2** are deep blue air-sensitive amorphous solids.

Infrared Spectra. Both compounds were characterized in absence of air by IR spectroscopy. The infrared spectra were recorded on a Bio-Rad IRFT spectrophotometer, in the 4000−250 cm^{-1} range, using pressed KBr pellets containing 1% in mass of the sample.

Magnetic Measurements. The magnetization measurements were performed using a SQUID magnetometer in the 2−350 K temperature range with a 50-Oe applied magnetic field. The field-dependent magnetization was measured at 10 K in the 0−5-kOe range.

X-ray Absorption and XMCD: Data Collection. X-ray absorption near-edge structures and X-ray magnetic circular dichroism were recorded at the K edges of chromium and vanadium in **1** and **2** at the energy dispersive absorption line of the DCI ring at LURE (Orsay). The samples were prepared under an argon atmosphere. The spectra were recorded using a Si(111) curved polychromator, focusing 70 cm away between the poles of a magnetic coil. Harmonics were rejected by a silica mirror located before the photodiode array, which is on the Rowland circle. Right circularly polarized photons were selected by positioning a 1 mm wide slit, 5.5 mm below the positrons' orbit plane. The circular polarization rate was 70%. The recording temperature was $T = 36$ K, in the ferrimagnetic phase of both magnets. The X-ray absorption spectra were recorded by measuring the photocurrent emitted by the photodiodes. They are normalized at the atomic absorbance. The energy scale ($E - E_0$) is relative to the metallic K edge ($E_0 = 5465$ eV for vanadium and $E_0 = 5989$ eV for chromium).

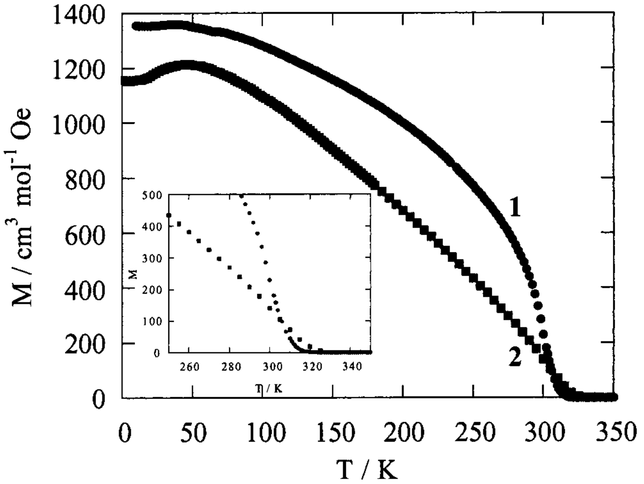

Figure 1. Thermal dependence of the magnetization of compounds **1** (●) and **2** (■) in an applied field ($H = 50$ Oe). The insert shows that compound **1** presents spontaneous magnetization down to 315 K and compound **2** down to 310 K.

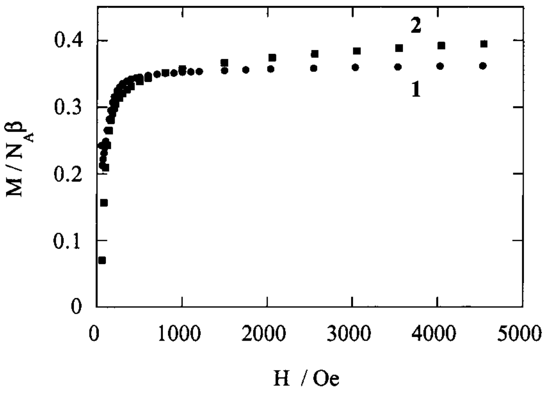

Figure 2. Magnetization versus applied field, up to $H = 5$ kOe at $T = 10$ K, for **1** (●) and **2** (■). The magnetization increases rapidly up to 500 Oe and then tends slowly to its saturation value: $M_s = 0.36N_A\beta$ for **1** and $M_s = 0.40N_A\beta$ for **2**.

In the electric dipolar approximation, reversing the magnetic field is equivalent to changing the helicity of the beam. [9] Hence, to record the XMCD spectra, the magnetic field ($H = 5$ kOe) was applied alternatively parallel and antiparallel to the direction of the photon beam. A first spectrum labeled $\sigma_{\uparrow\uparrow}$ was registered with the magnetic field parallel to the propagation vector of the photons. Then a second spectrum, labeled $\sigma_{\uparrow\downarrow}$, was recorded with the magnetic field applied in the opposite direction. The XMCD signal was taken as the difference ($\sigma_{\uparrow\uparrow} - \sigma_{\uparrow\downarrow}$) between the two spectra.

Results

The thermal variation of the magnetization for **1** and **2** is shown in Figure 1. A transition to a magnetically ordered state occurs at 310 K for **1** and 315 K for **2**. The insert displays an expanded view of the transition range. The magnetization versus applied field is given in Figure 2 for both compounds. The magnetization increases rapidly with applied field and reaches a saturation value $M_S/N_A\beta$ equal to 0.36 for **1** and 0.40 for **2** at 5 kOe (Table 1).

The isotropic X-ray absorption near-edge spectra (XANES) and the dichroic signals (XMCD, ×100) at the K edges of chromium and vanadium are displayed in Figures 3 and 4 for **1** and in Figures 5 and 6 for **2**. Figures 3 and 5 correspond to the chromium K edges and Figures 4 and 6 to the vanadium K

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(7) Elemental analysis for **1**: Found: C, 16.9%; N, 20.4%; H, 2.1%; V, 17.3%; Cr, 12.5%; S, 2.7%; K, 0.6%. Calculated: C, 18.1%; N, 21.1%; H, 2.2%; V, 18.6%; Cr, 13.0%; S, 2.9%; K, 0.6%.

(8) Elemental analysis for **2**: Found: C, 15.6%; N, 18.4%; H, 1.2%; V, 11.5%; Cr, 10.8%; S, 0.2%. Calculated: C, 15.6%; N, 18.2%; H, 1.7%; V, 12.0%; Cr, 11.3%; S, 0.2%; Cs, 25.7%. Cs data are lacking. The uncertainty in the formula of **2** is larger than in **1**.

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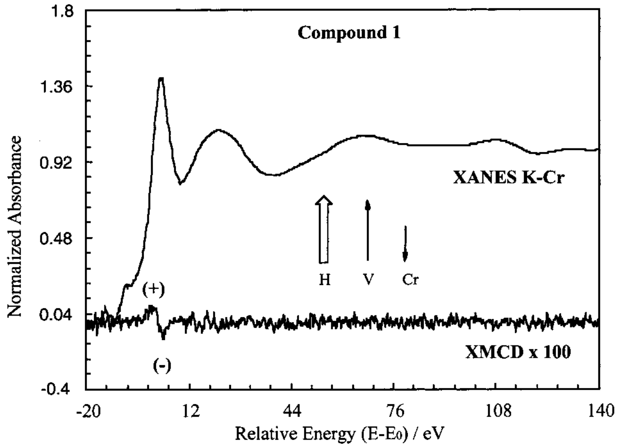

Figure 3. Chromium K edge in **1**: isotropic and dichroic absorption spectra.

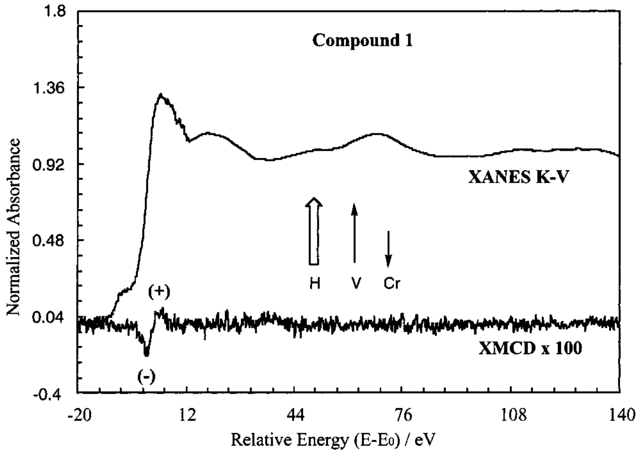

Figure 4. Vanadium K edge in **1**: isotropic and dichroic absorption spectra.

Table 1. Characteristics of Compounds **1** and **2**[a]

	compd **1**	compd **2**
molar weight/g mol^{-1}	274.4	424.4
%V^{II}/V	0.45	0.66
z	0.69	0.92
calcd $M_T/N_A\beta$	−0.36	+0.42
obsd $M_S/N_A\beta$	0.36	0.40

[a] Molar weight per formula unit; %V^{II}/V, percentage of V^{II}; z, stoichiometric ratio Cr/V between chromium and vanadium; calculated M$_T$ derived from eq 1; observed M_S derived from experimental measurements (Figure 2).

edges. Inserts display the orientation of the local magnetic moments of the metallic centers in the applied magnetic field as discussed below. Table 2 provides a schematic description of the dichroic signals of compounds **1** and **2**, at the chromium and vanadium edges and, for the sake of comparison, the corresponding data for two other molecule-based magnets: (i) $Cs^INi^{II}[Cr^{III}(CN)_6]\cdot 2H_2O$ (**3**), known to be ferromagnetic with T_C at 90 K;[1b] in **3**, all the magnetic moments, the ones of nickel(II) (d^8), $S = 1$, and the ones of chromium(III) (d^3), $S = {}^3/_2$, are parallel and aligned in the field; (ii) $Cs^IMn^{II}[Cr^{III}(CN)_6]\cdot 2H_2O$ (**4**), known to be ferrimagnetic with T_C at 90 K;[10] in **4**, the magnetic moments aligned parallel to the magnetic field are the ones of Mn(II) (d^5, $S = {}^5/_2$), whereas the ones of chromium(III) are antiparallel to the field.

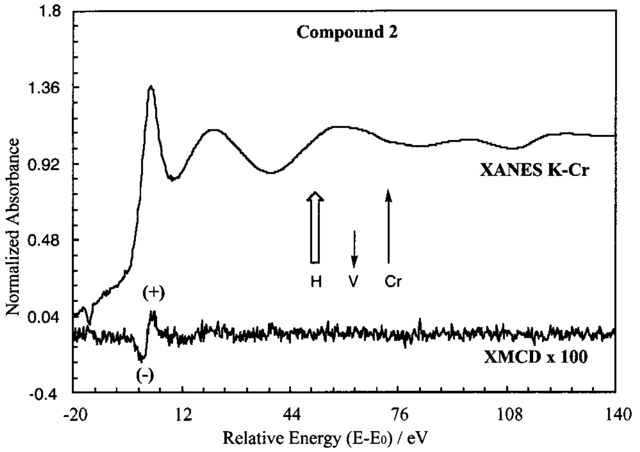

Figure 5. Chromium K edge in **2**: isotropic and dichroic absorption spectra.

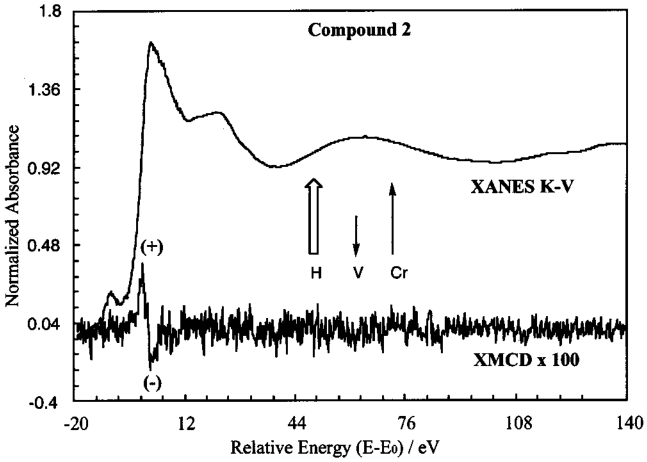

Figure 6. Vanadium K edge in **2**: isotropic and dichroic absorption spectra.

Discussion

Next, we discuss three points: (1) the values of the magnetic moments due to the antiferromagnetic coupling between chromium and vanadium neighbors, (2) the near-edge X-ray absorption spectra, and (3) the XMCD spectra and their physical significance to understand the magnetization of the samples.

(1) Magnetic Moments in 1 and 2. The general formula of this family of room-temperature molecule-based magnets is $C^I_yV[Cr^{III}(CN)_6]_z\cdot nH_2O$, z generally varying between ${}^2/_3$ and 1 and y between 0 and 1. The oxidation state of vanadium (II, III, or IV) was deduced from (i) the elemental analysis of the compounds, (ii) the electroneutrality, (iii) the shape of the $\nu_{\mathrm{asC}\equiv\mathrm{N}}$ band in the IR spectrum and its shift to higher energies when going from $Cr^{III}{-}C{\equiv}N{-}V^{II}$ (2110 cm^{-1}) to $Cr^{III}{-}C{\equiv}N{-}V^{IV}O$ (2180 cm^{-1}),[11] (iv) the presence of the $\nu_{\mathrm{as(V^{IV}O)}}$ band at 981 cm^{-1}, and (v) the presence of a peak of medium intensity in the preedge of the X-ray absorption spectrum at the vanadium K-edge: when vanadium changes from octahedral V(II) to square pyramidal V(IV), the local symmetry of vanadium changes from O_h to C_{4v} and the transition becomes allowed.[12]

The formula of **1** and **2** allows calculation of the resulting magnetic momentum, $M_T/N_A\beta$, per formula unit (in Bohr magnetons; N_A, Avogadro constant; β, Bohr magneton). The

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Table 2. Schematic Description of the Dichroic Signal at the K Metallic Edges in Compounds **1**, **2**, **3**, and **4** and Orientation of the Local Moments of the Metallic Ions in the Applied Field

			Dichroic signal for Chromium		Dichroic signal for Vanadium		Dichroic signal for Nickel or Manganese	
Compound number	Abbreviation	Short range interaction	Signal description	Moment orientation in the field [a]	Signal description	Moment orientation in the field [a]	Signal description	Moment orientation in the field [a]
1	$VCr_{0.69}$	AF	(+ -)	↓[e]	(- +)	↑[d]		
2	$Cs_{0.82}VCr_{0.96}$	AF	(- +)	↑[d]	(+ -)	↓[e]		
3	CsNiCr	F	(- +)	↑[b]			(- + -)	⇑[c]
4	CsMnCr	AF	(+ -)	⇓[c]			(- +)	↓[b]

[a] Applied field up. [b] Black wide arrows, known orientation of the larger moments (Cr) in the ferromagnet **3** and of the larger moments (Mn) in the ferrimagnet **4**. [c] White wide arrows, known orientations of the smaller moments in **3** and **4**. [d] Black long arrows, orientation of the larger moments in **1** and **2**, deduced from the dichroic signal as discussed in the text. [e] Black short arrows, orientation of the corresponding smaller moments in **1** and **2**.

coupling between the vanadium and the chromium ions is known to be antiferromagnetic:[4] it implies t_{2g} electrons only on both ions; the t_{2g} orbitals overlap and interact strongly since they are diffuse and fit in energy. In these conditions:

$$M_T/N_A\beta = M_{Cr} - M_V = -[zg_{Cr}S_{Cr} - g_VS_V\,] = -g\left[\frac{3z}{2} - S_V\right] = -2\left[\frac{3z}{2} - S_V\right] \quad (1)$$

where we approximate g to 2 for the two metallic ions. Therefore, the sign of M_T can change depending on the absolute value of the local magnetization M_{Cr} and M_V. Two situations may arise: $|M_{Cr}| > |M_V|$, then the chromium magnetic moments are parallel to the applied magnetic field and the vanadium moments at the opposite; $|M_V| > |M_{Cr}|$, then the vanadium moments are parallel to the field and the chromium moments at the opposite.

We apply (1) to compounds **1** and **2**:

$C^I_yV^{II}_{\alpha}V^{III}_{1-\alpha}[Cr^{III}(CN)_6]_z{\cdot}nH_2O$ for **1** and

$$M_T = -2\left[\frac{3z}{2} - \frac{3\alpha}{2} - \frac{2}{2}(1-\alpha)\right]$$

$$M_T = -(3z - \alpha - 2) \quad (2)$$

$C^I_yV^{II}_{\alpha}(V^{IV}O)_{1-\alpha}[Cr^{III}(CN)_6]_z{\cdot}nH_2O$ for **2** and

$$M_T = -2\left[\frac{3z}{2} - \frac{3\alpha}{2} - \frac{1}{2}(1-\alpha)\right]$$

$$M_T = -(3z - 2\alpha - 1) \quad (3)$$

The calculated M_T value is positive for **1** ($M_T = +\ 0.36N_A\beta$) and negative for **2** ($M_T = -\ 0.42N_A\beta$). Table 1 reports the experimental and calculated M_T parameters, the values of z, and V^{II}/V ratios for **1** and **2**. The absolute values are in good agreement with the experimental ones. The crucial difference between the two compounds is the sign of M_T, influenced by the balance between the values of z (Cr^{III}/V ratio) and the ratio V^{II}/V. It appears remarkable that, depending on the synthetic conditions, two compounds of general formula $C^I_yV[Cr^{III}(CN)_6]_z{\cdot}nH_2O$ may have similar macroscopic magnetic behavior arising from opposite local magnetization characteristics.

The spin value can be represented in a three-dimensional space, depending on the value of α varying between 0 and 1 and z varying between $^2/_3$ and 1. The spin values are described by planes, represented in Figure 7a for eq 2 and Figure 7b for eq 3. In Figure 7a the maximum spin value can be 1, which is reached by the compounds $V^{III}[Cr^{III}(CN)_6]{\cdot}nH_2O$ and $C^IV^{II}[Cr^{III}(CN)_6]_{2/3}{\cdot}n'H_2O$. In Figure 7b, the maximum spin value is foreseen in $C^I(V^{IV}O[Cr^{III}(CN)_6]_{2/3}{\cdot}nH_2O$. For both situations, the bold line represents systems where the total spin is zero, i.e. antiferromagnetic compounds. According to the convention of eq 1, the compounds above these lines have a resulting spin direction aligned with the one of the chromium ions. Hence, **2** belongs to this part of plane in Figure 7b. On the contrary, **1** in Figure 7a belongs to the part of the plane where the resulting spin direction is the one of the vanadium ions. In the compound $A^{-I}V^{III}Cr^{III}_{2/3}$ (Figure 7a), A^{-I} is an anion ensuring electroneutrality.

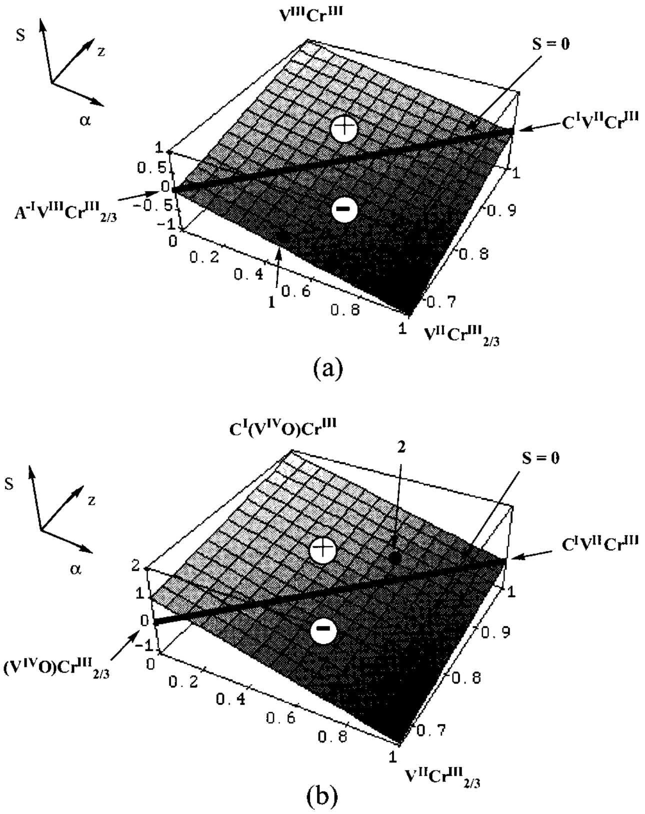

Figure 7. Variations of the spin values S versus z and α parameters for compounds of formula $C^I_yV^{II}_{\alpha}V^{III}_{1-\alpha}[Cr^{III}(CN)_6]_z{\cdot}nH_2O$ (a) and $C^I_yV^{II}_{\alpha}(V^{IV}O)_{1-\alpha}[Cr^{III}(CN)_6]_z{\cdot}nH_2O$ (b). In panel a, **1** is in the part of the plane where the total spin has the same direction as the vanadium spins. In panel b. **2** is located in the part of the plane where the total spin has the same direction as the chromium spins.

We turn now to XAS and XMCD data to check these hypotheses.

(2) X-ray Absorption Spectra (XANES). In a simplified one-electron picture, with a dipolar electric operator, in linearly polarized light, the K-edges XANES structures correspond to transitions of the 1s photoelectron to p-symmetry bound and continuum states according to the usual atomic selection rules ($\Delta S = 0$, $\Delta L = \pm 1$, $\Delta J = 0, \pm 1$) and the Fermi golden rule: $\mu(E) \propto \langle \Psi_{\mathrm{exc}}|O_{\mathrm{dip}}|\Psi_{\mathrm{ground}}\rangle^2$ (the Ψ_{ground} initial state is totally symmetric (1s); allowed transitions are the ones when the Ψ_{exc} final state of the excited electron has the same symmetry as $O_{\mathrm{dip}}-x,y,z-$). The isotropic spectra at the chromium edge in **1** and **2** (Figures 4 and 6) and at the vanadium edge in **1** (Figure 5) display the main features expected in a K edge of a transition metal ion in a nearly octahedral surroundings (O_h):

(1) weak preedge signals (dipole forbidden transitions 1s → molecular orbitals containing 3d, t_{2g} and e_g symmetries);

(2) intense white line (dipole allowed transitions 1s → molecular orbitals containing p, t_{1u} symmetry, abbreviated as 4p in the following);

(3) multiple-scattering structures close after the white line, due to the alignment of the $Cr^{III}-C\equiv N-V$ units;

(4) then, at higher energies, beginning of the EXAFS oscillations.

In the rising edge, the shoulder can be assigned to an allowed transition toward t_{1u} symmetry molecular orbitals containing 4p and $\pi^*(C\equiv N)$ levels.

The two isotropic chromium K edges are quasi-identical, which confirms the presence of the $[Cr^{III}(CN)_6]$ molecular precursor in both compounds.

The vanadium K edge spectrum in **2** is different since the preedge displays a medium-intensity well-defined band. This band is a clear signature of the presence of VO(IV) in the sample, confirmed by IR spectrum. It is due to allowed transitions to the molecular orbitals mixing 3d and 4p metallic orbitals thanks to C_{4v} symmetry, C_4 along the VO axis (namely, 1s → z^2-based MO (a_1 symmetry)−z polarized−and 1s → xz,yz-based MOs (e symmetry)−x,y polarized).

(3) X-ray Magnetic Dichroism Spectra (XMCD). The interest of the technique for the study of magnetic materials comes from the fact that (i) each atomic species and each orbital level can be probed selectively by varying the excitation energy; (ii) in the presence of a magnetic field (either applied or from exchange origin), the absorption cross section of a metallic absorber in a magnetically ordered compound depends on the polarization of the light: in a magnetic field, the M_J components of a given level J are split; the selection rules for the M_J quantum number are $\Delta M_J = 0$ for linear polarization; $\Delta M_J = -1$ for left circularly polarized light and $\Delta M_J = +1$ for the right polarized one. The difference between the left and right spectra gives the dichroic signal, directly proportional to the local magnetic moment.[13] The dichroic signal is expected for allowed transitions ($\Delta L = \pm 1$; i.e., here in 1s−4p transitions, in the white line energy range); since the operator is dipolar electric (no magnetic component), the magnetic dichroic signal at the K edge can appear only if the orbital and spin components are coupled, i.e., here in the presence of spin−orbit coupling in the 4p metallic levels, in the excited state ($1s^1 3d^n 4p^1$ electronic configuration). Then, the exchange interaction of the 4p excited electron with the 3d electrons will provide information about the local magnetic properties of the photon absorber [14] and especially about the direction of the local magnetic moment due to the unpaired d electrons.

Like the XAS signal, the XMCD signal appears whatever the shape of the sample (crystals, powders, etc.). Information on the local spins can be obtained by a technique such as spin-polarized neutron diffraction, but it requires long-range structural order and large single crystals. XMCD is better adapted for poorly organized materials.

A dichroic signal of weak intensity (0.15−0.30% of the isotropic spectra) is present in our compounds at the four edges, in the energy range corresponding to the allowed transition to the p-symmetry levels of the metal. The small intensity of the K edge signal, compared to the L edges one, is due to the absence of spin−orbit coupling in the 1s level and to the weakness of the spin−orbit coupling in the final state.[15] At the $L_{2,3}$ edges the XMCD signals can be as large as 60% of the atomic cross section, since the L edge is a direct probe of the d states ($\Delta L = +1$); on the contrary, XMCD signals at K edges are never larger than a few 0.1%, which is verified here. It is not our purpose to give a detailed interpretation of the dichroic signals in our compounds nor to reproduce them by calculations. This is a work per se, which necessitates computation of spin-dependent wave functions in the materials [16] and the use of such wave functions in multiple scattering programs.[17] The phenomenological use of the dichroic spectra is nevertheless worthy of interest since, as shown above, the dichroic signal is directly related to the direction of the magnetic moments due to the 3d unpaired electrons.

The macroscopic magnetization data demonstrate that the spins of chromium (d^3) and vanadium (d^1, d^2, and d^3) are antiferromagnetically coupled, as shown in the inserts of Figures 3−6. This macroscopic interpretation is fully confirmed by the local dichroic signals:

In **1**, at the chromium K edge, the dichroic signal is first positive and then negative (+ −), whereas at the vanadium K edge, it behaves at the opposite (− +) (Table 2). Since the 4p orbitals have only one electron in the excited state, the sign of the 4p spin−orbit coupling is the same in the chromium and in the vanadium ions. The inversion of the dichroic signal (+ −) in chromium compared to vanadium (− +) is therefore a clear demonstration of the local antiferromagnetic coupling between V and Cr in the ferrimagnet **1**.

In **2**, we reach exactly the same conclusion since the dichroic signal is once more reversed in the chromium (− +) compared to the vanadium (+ −).

The new and important fact is that, for a given edge, the general shape of the dichroic signal is exactly the opposite in compounds **1** and **2**, as shown in Figures 3−6 and in Table 2. This is the experimental proof that the larger magnetic moment, aligned with the magnetic field, is borne in one case by the

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vanadium ions and in the other by the chromium ions. The change in the stoichiometry is followed by a slight change in the macroscopic magnetization but, above all, by the change in the nature of the metallic species bearing the larger magnetic moment.

It is even possible to go further and to determine experimentally which is the metallic ion bearing the larger magnetic moment. For that, we use the results obtained in the ferromagnetic $Cs^{I}Ni^{II}[Cr^{III}(CN)_6]\cdot 2H_2O$ (**3**), where the moments of the nickel and of the chromium ions are parallel and aligned in the field. The shape of the chromium dichroic signal is $(- +)$[18] and gives the answer to the above question: a chromium $(- +)$ dichroic signal corresponds to a chromium moment aligned parallel to the field. In a ferrimagnet such as **2**, chromium is therefore bearing the larger magnetic moment. It is then trivial to conclude that, in **1**, the vanadium ions bear the larger magnetic moment [$(- +)$ dichroic signal] and the chromium the weaker one [$(+ -)$ dichroic signal]. Furthermore, the dichroic signals of chromium and manganese observed in the ferrimagnet $Cs^{I}Mn^{II}[Cr^{III}(CN)_6]\cdot 2H_2O$[18] (**4**), where the majority spins are the ones of Mn(II) (d^5 $S = {}^5/_2$), are fully consistent with the preceding demonstration (Table 2): the manganese dichroic signal $(- +)$ shows that the manganese moments are parallel to the magnetic field. The chromium dichroic signal $(+ -)$ shows that its moment lies antiparallel to the field.

Conclusion

Prussian blue analogues of general formula $C^{I}A[B^{III}(CN)_6]_z\cdot nH_2O$ are known to be high-T_C molecule-based magnets and to present magnetooptical properties.[1e,19] Here we reported on two new room-temperature magnets belonging to this family, able to change the nature of the bearer of the larger magnetic moment by changing the chemical composition with the same A/B pair. The phenomenon is different from the one observed in the ternary compounds $Ni^{II}{}_xMn^{II}{}_{1-x}[Cr^{III}(CN)_6]_q\cdot nH_2O$, with T_C values below 80 K.[20]

Among the two techniques able to directly determine the orientation of the spins on local metallic centers, spin-polarized neutron diffraction and XMCD, the first one was nonapplicable since the compounds were amorphous powders whereas XMCD was able to give the required qualitative answer.

First, a dichroic signal was detected at all the edges: the 4p Cr and V orbitals appear to be spin-polarized. Second, the sign of the dichroic signal was used to determine locally (i) the antiferromagnetic coupling between V and Cr ions and (ii) the reversal of the magnetic moments: the vanadium ions bear the larger magnetic moment in **1** and the chromium ions in **2**. This is the first time that such an inversion of the local magnetic moments is pointed out by XMCD in molecule-based magnets.

The study confirms (i) the usefulness and the ability of XMCD to determine the spin orientation on each metal ion in bimetallic ferri- or ferromagnets; (ii) the ability of the vanadium−chromium room temperature ferrimagnets to widely change their magnetic properties by varying their chemical composition. Here, compounds **1** and **2** have enhanced magnetization at saturation compared to the first reported material. If the addressing of the resulting magnetic moment can be reversibly induced by chemical oxidation and reduction in the same compound, the property could be used in chemical sensors.

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