

Sol–Gel Synthesis of $\text{KV}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$: A Crystalline Molecule-Based Magnet with a Magnetic Ordering Temperature above 100 °C

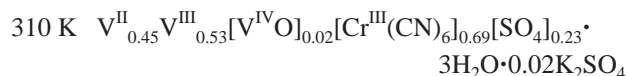
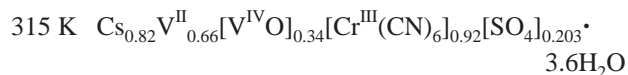
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Recently, there has been much interest in the synthesis of molecule-based magnets, which are magnets whose solid-state structures consist of arrays of molecular units.^{1,2} Such solids do not at present have real-world uses, in part because none of them possesses a key characteristic: for most commercial applications, a magnet must retain its magnetism well above room temperature. Of the four molecule-based magnets that remain magnetic at room temperature, one decomposes at 350 K,³ and three demagnetize near 315 K.^{4,5} All four of these solids are amorphous, and their solid state structures are unknown, although the latter three probably adopt a structure like that of the pigment Prussian blue. We now describe the use of sol–gel methods to synthesize several crystalline molecule-based magnets with the Prussian blue structure. The gelation process appears to be important to the growth of the crystalline phase. Most notable among the current results is the discovery of a molecule-based magnet, $\text{KV}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$, with the unprecedented magnetic ordering temperature of 376 K (103 °C).

The four known molecule-based magnets that keep their magnetism at room temperature are listed below, along with the temperatures at which the magnetism is lost:



Crystalline samples of materials related to the above solids should have even higher magnetic ordering temperatures. We have focused our efforts on relatives of the latter three compounds in the list. In an effort to develop a synthetic route that would afford crystalline Prussian blue analogues that contain V^{II} and Cr^{III} centers, we have investigated the use of starting materials with large organic counterions such as trifluoromethanesulfonate, OTf[−], and tetra(ethyl)ammonium, NET_4^+ .^{6–8} These counterions were initially chosen because they are too large to be incorporated into the Prussian blue structure, so that the contents of the cuboctahedral interstitial sites could be controlled. As it turns out, a more important feature may be their hydrophobic natures, which may

increase the degree of ion pairing in solution and promote the formation of a gel.

Thus, treatment of aqueous solutions of $\text{V}^{\text{II}}(\text{OTf})_2$ ⁹ with $[\text{NET}_4]_3[\text{Cr}^{\text{III}}(\text{CN})_6]$ ¹⁰ under anaerobic conditions affords a dark blue gel after about 10 min. The gel forms only if the reactant concentrations are above a certain threshold; for our experiments, the reagent concentrations were 0.02–0.06 M. After 24 h, the gel becomes less viscous and takes on the appearance of a suspension. The suspended solids were collected by centrifugation and washed with water to afford $\text{V}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.66} \cdot 3.5\text{H}_2\text{O} \cdot 0.1[\text{NET}_4][\text{OTf}]$ (**1**).¹¹

Addition of alkali metal cations to the reaction solution affords products with V to Cr ratios that are close to 1:1 rather than 2:3. If the reagent concentrations are sufficiently high, these reactions also form gels within 10 min. Provided that the gel forms and the solutions are allowed to stand for at least 24 h, then crystalline products are obtained. Thus, if the reaction above is carried out in the presence of 4.5 equiv of CsOTf, then the cesium salt $\text{Cs}_{0.82}\text{V}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.94} \cdot 3\text{H}_2\text{O} \cdot 0.4[\text{NET}_4][\text{OTf}]$ (**2**) is isolated.¹¹ A similar reaction of $\text{V}(\text{OTf})_2$ with the potassium salt $\text{K}_3[\text{Cr}(\text{CN})_6]$ leads to the product $\text{KV}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 2\text{H}_2\text{O} \cdot 0.1\text{KOTf}$ (**3**).¹¹

Cyanide hydrogels have previously been reported to form with the following combinations of species: $\text{Pd}^{\text{II}}/\text{Fe}(\text{CN})_6^{3-}$, $\text{Pd}^{\text{II}}/\text{Co}(\text{CN})_6^{3-}$, and $\text{Sn}^{\text{IV}}/\text{Fe}(\text{CN})_6^{4-}$.^{12–14} Our observations are consistent with the conclusions of these earlier studies: the gelation time depends on the nature of the cations and anions, the stoichiometry of the reaction solutions, and the concentrations of the reactants employed.

Compounds **1–3** are crystalline (Figure 1), and their diffraction patterns can be indexed to face-centered cubic (fcc) unit cells with lattice constants of 10.54, 10.65, and 10.55 Å, respectively. The widths of the diffraction peaks¹⁵ show that the average crystallite sizes are 150, 75, and 90 Å for **1**, **2**, and **3**, respectively.

The infrared spectra of **1–3** exhibit intense C–N stretching bands at 2117, 2120, and 2117 cm^{-1} , respectively. No features are present in the 900–1000 cm^{-1} regions, and thus vanadyl ($\text{V}=\text{O}$) units are absent.¹⁷ Exposure to air for 10 min causes intense new bands to appear at 2173 cm^{-1} for **1**, 2175 cm^{-1} for **2**, and 2169 cm^{-1} for **3**. The new bands signal the oxidation of the V^{II} centers; these bands are weak or absent in the as-isolated materials, which must therefore contain few oxidized vanadium centers. Longer air exposures eventually cause the growth of an intense vanadyl ν_{VO} stretch near 980 cm^{-1} .

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(11) Anal. Calcd for $\text{C}_{4.86}\text{H}_9\text{N}_{4.06}\text{O}_{3.8}\text{S}_{0.1}\text{F}_{0.3}\text{Cr}_{0.66}\text{V}$ (**1**): C, 20.9; H, 3.2; N, 20.4; Cr, 12.3; V, 18.3. Found: C, 19.9; H, 2.4; N, 18.7; Cr, 12.0; V, 18.2. Anal. Calcd for $\text{C}_{9.24}\text{H}_{14}\text{N}_{6.04}\text{O}_{4.5}\text{S}_{0.4}\text{F}_{1.2}\text{Cs}_{0.82}\text{VCr}_{0.94}$ (**2**): C, 21.3; H, 2.7; N, 16.2; Cr, 9.4; V, 9.8. Found: C, 21.3; H, 2.0; N, 16.1; Cr, 9.4; V, 9.8. Anal. Calcd for $\text{C}_{6.1}\text{H}_4\text{N}_6\text{O}_{2.3}\text{S}_{0.1}\text{F}_{0.3}\text{CrVK}_{1.1}$ (**3**): C, 20.7; H, 1.1; N, 23.8; Cr, 14.7; V, 14.5; K, 12.2. Found: C, 19.8; H, 1.0; N, 20.8; Cr, 15.0; V, 14.6; K, 12.4.

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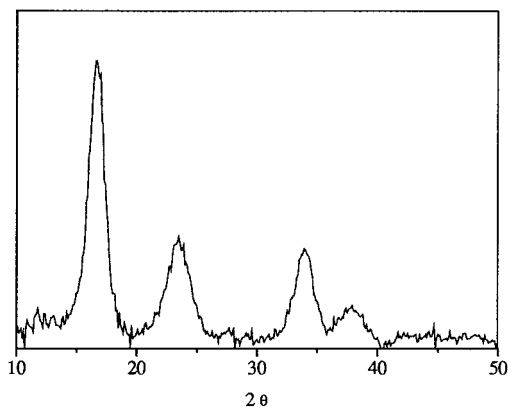


Figure 1. X-ray diffraction pattern of $\text{KV}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 2\text{H}_2\text{O} \cdot 0.1[\text{NEt}_4][\text{OTf}]$ (**3**). A baseline-corrected spectrum is shown. The four main peaks are the 200, 220, 400, and 420 reflections.

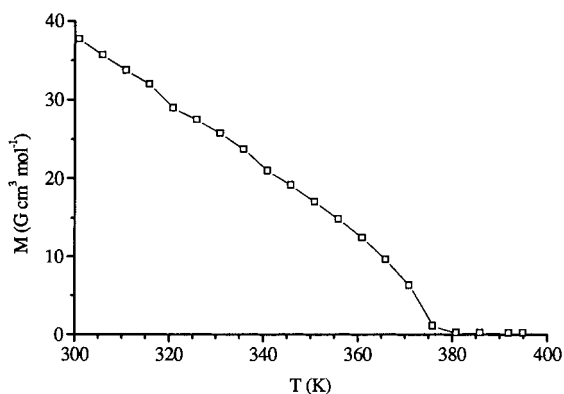


Figure 2. Temperature dependence of the zero-field cooled magnetization of $\text{KV}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 2\text{H}_2\text{O} \cdot 0.1\text{KOTf}$ (**3**) at an applied field of 50 G.

The magnetic ordering temperatures of **1–3**, which were deduced from the variable temperature magnetization curves, are 330, 337, and 376, respectively (Figure 2). For **1** and **3**, the magnetic ordering temperature decreases slightly after the samples are heated. Fresh samples of **1** order magnetically at 330 K, but the ordering temperature (T_N) decreases to 320 K after the sample is heated to 350 K, and to 310 K after multiple heating cycles. The infrared spectrum of **1** does not change when the sample is heated, and thus the change in ordering temperature is probably not a consequence of linkage isomerism.^{2,3,17,18} Instead, dehydration is probably responsible for the decrease in T_N when the samples are heated. For a presumably similar reason, the ordering temperature of **3** decreases from 376 to 365 K upon repeated heating of the material to 400 K. For **2**, the magnetic ordering temperature remains unchanged upon heating the sample to 350 K.

The magnetic moments per formula unit (μ_{eff}) measured 25 K above their magnetic ordering temperatures are 4.7, 3.4, and 3.0 μ_B for **1–3**, respectively. These values are lower than those of 5.0, 5.4, and 5.5 μ_B calculated from their chemical formulas, assuming that $g = 2$ and that the V^{II} and Cr^{III} spins are completely randomized. The experimental values for μ_{eff} suggest that short-range antiferromagnetic interactions persist in these solids above T_N , as is common for ferrimagnets.

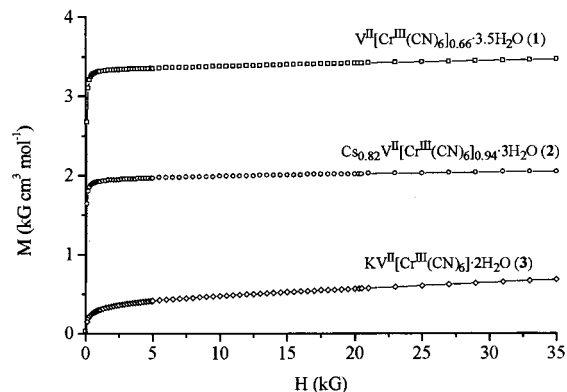


Figure 3. Saturation magnetization curves for **1–3** at 5 K.

The saturation magnetizations of **1–3** in a 40 kG applied field are 3.5, 2.2, and 0.7 $\text{kG cm}^3 \text{mol}^{-1}$, respectively (Figure 3). The values calculated from their chemical formulas, assuming that the magnetic interactions between adjacent metal centers are antiferromagnetic, are 5.7, 1.0, and 0 $\text{kG cm}^3 \text{mol}^{-1}$; these values follow the same order as those found experimentally. Because compound **3** contains nearly-equal numbers of d^3 V^{II} and Cr^{III} centers, the spins are almost entirely canceled in the magnetically ordered state. A 4% deviation from exact 1:1 stoichiometry, oxidation of about 12% of the V^{II} centers to V^{III} , or oxidation of about 6% of the V^{II} centers to V^{IV} could account for the residual magnetization. Compounds **1–3** exhibit hysteretic behavior, having coercive fields of 10, 15, and 165 G and remnant magnetizations of 570, 750, and 220 $\text{G cm}^3 \text{mol}^{-1}$ at 5 K, respectively. The small coercive fields are consistent with the presence of magnetically isotropic ions such as V^{II} and Cr^{III} in a highly symmetrical cubic environment. The coercive fields are even smaller just below the magnetic ordering temperatures (3.5 G for **2** at 330 K; 4 G for **3** at 360 K), and the hysteresis loops are completely closed at 350, 350, and 380 K for **1–3**, respectively.

Compound **3** remains magnetic to higher temperatures than does any other molecule-based magnet described to date. The high ordering temperature is a consequence of several factors. First, it contains V^{II} centers, which are strong π -donors and thus are unusually effective in delocalizing spin density onto the cyanide bridges.⁶ Second, the 1:1 V to Cr ratio means that the average number of Cr neighbors about each V ion (and vice versa) is six, the maximum possible for these ions; this feature is advantageous because theory predicts that T_N for a ferrimagnet should be proportional to the number of nearest neighbors.¹⁹ Third, the material is crystalline, which we tentatively attribute to the slow growth of the phase from the gel. Fourth, the content of the interstitial sites in the fcc structure has been made more uniform by controlling the sizes of the ions present in solution during the synthesis.

For the first time, a molecule-based magnet that retains its magnetism at 100 °C has been prepared. This result is an important step in the conversion of molecule-based magnets from laboratory curiosities to practical materials.

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