Sol–Gel Synthesis of KVII[CrIII(CN)6]·2H2O: 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. Such solids do not at present have real-world uses, in part because none of them possess 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, and three demagnetize near 315 K. 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, KVII[CrIII(CN)6]·2H2O, 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:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Compound</th>
</tr>
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<tbody>
<tr>
<td>~350 K</td>
<td>V(tene)2·0.5CH2Cl2</td>
</tr>
<tr>
<td>315 K</td>
<td>Cs0.82VII1.66[VIVO]0.32[CrII(CN)6]0.92SO40.209*3.6H2O</td>
</tr>
<tr>
<td>315 K</td>
<td>K0.42VII0.58[CrIII(CN)6]0.86·2.8H2O</td>
</tr>
<tr>
<td>310 K</td>
<td>K0.45VIII0.53[VIVO]0.62[CrIII(CN)6]0.35SO40.23*3H2O·0.02KSO4</td>
</tr>
</tbody>
</table>

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 VII and CrIII centers, we have investigated the use of starting materials with large organic counterions such as trifluoromethanesulfonate, OTf−, and tetra(ethyl)ammonium, NEt4+.

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 Cs0.82VII[CrIII(CN)6]0.92H2O·0.4[NEt4][OTf] (2) is isolated. A similar reaction of V(OTf)2 with the potassium salt K3[Cr(CN)6] leads to the product KVII[CrIII(CN)6]·2H2O·0.1KOTf (3).

Cyanide hydrogels have previously been reported to form with the following combinations of species: Pd(II)Fe(CN)63−, Pd(II)Co(CN)63−, and Sn(II)Fe(CN)63−.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 (V=O) units are absent. 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 VII 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 νν=O stretch near 980 cm−1.

2. Verdaguer, M.; Girolami, G. S., manuscript in preparation.
11. Anal. Calcd for C4.86H9N4.06O3.8S0.1F0.3Cr0.66V(III): C, 20.7; H, 1.1; N, 23.8; Cr, 12.0; V, 18.3. Found: C, 20.9; H, 3.2; N, 20.4; Cr, 12.3; V, 18.4.
temperature remains unchanged upon heating the sample to 350 K. Heating of the material to 400 K. For a presumably similar reason, the ordering temperature is probably responsible for the decrease in $T_N$ when 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. 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 ($\mu_{eff}$) measured 25 K above their magnetic ordering temperatures are 4.7, 3.4, and 3.0 $\mu_B$ for 1–3, respectively. These values are lower than those of 5.0, 5.4, and 5.5 $\mu_B$ 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 $\mu_{eff}$ suggest that short-range antiferromagnetic interactions persist in these solids above $T_N$, as is common for ferrimagnets.

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. 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.

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