

## Molecule-Based Magnets Constructed from Cyanometalate Building Blocks

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Magnetic solids have numerous and important technological applications: they find wide use in information storage devices, microwave communications systems, electric power transformers and dynamos, and high-fidelity speakers.<sup>1-3</sup> By far the largest application of magnetic materials is as information storage media, and the annual sales of computer diskettes, compact disks, optical disks, recording tape, and related items exceed those of the celebrated semiconductor industry.<sup>3-5</sup> The demand for higher bit-density information storage media and the emergence of new technologies such as magneto-optic devices makes it crucial to expand the search for entirely new classes of magnetic materials.<sup>2,3</sup>

In response to the increasing demands being placed on the performance of magnetic solids, over the last decade or so there has been a surge of interest in molecule-based magnets.<sup>6-10</sup> In such solids, discrete molecular building blocks are assembled, with their structures intact, into 1-, 2-, or 3-dimensional arrays. One of the attractive features of molecular magnets is that, by choosing appropriate building blocks, the chemist can exert considerable control over the connectivity and architecture as well as the resulting magnetic properties of the array. The local exchange interactions, which can be specifically tailored through judicious choice of appropriate molecular building blocks, dictate the bulk magnetic behavior of the solid. By choosing molecular building blocks whose magnetic orbitals are of specific symmetries, and linking the building blocks into arrays with favorable geometric relationships between the building blocks, the synthetic chemist can exert powerful control over the properties of new molecule-based magnetic materials.

Solids with the Prussian blue structure (Figure 1) are especially attractive as

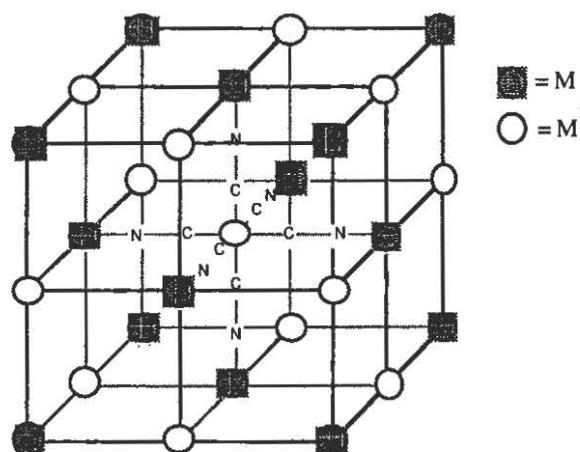


Figure 1

candidates for new molecule-based magnets for several reasons: they can be easily prepared at room temperature from well-characterized and chemically stable  $[M(CN)_6]^{n-}$  building blocks, the

metal centers are linked covalently into a cubic 3D network, and a wide range of metals with different spin states and oxidation states can be substituted into the structure.<sup>11-17</sup> Furthermore, the bridging cyanide ligand can promote strong magnetic exchange couplings between paramagnetic centers. These features allow considerable control over the nature and magnitude of the local magnetic exchange interactions.

We have prepared the first Prussian blue magnet containing  $\text{Ti}^{\text{III}}$  centers,  $\text{Ti}^{\text{III}}[\text{Cr}^{\text{III}}(\text{CN})_6]\cdot\text{H}_2\text{O}$ . Despite having only one  $d$  electron on the  $\text{Ti}^{\text{III}}$  center and the consequent small number of exchange pathways, this crystalline ferrimagnet has a respectably high ordering temperature of 255 K.

Addition of the triflate salt  $\text{V}(\text{O}_3\text{SCF}_3)_2$  to  $[\text{NEt}_4]_3[\text{Cr}(\text{CN})_6]$  affords the Prussian blue analogue  $\text{V}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.66}\cdot 3.5\text{H}_2\text{O}\cdot 0.1[\text{NEt}_4][\text{OTf}]$ . Interestingly, this synthesis proceeds by means of a gel stage. Variations of this procedure afford the related materials  $\text{Cs}_{0.82}\text{V}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.94}\cdot 3\text{H}_2\text{O}\cdot 0.4[\text{NEt}_4][\text{OTf}]$  and  $\text{KV}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]\cdot 2\text{H}_2\text{O}\cdot 0.1\text{KOTf}$ . These ferrimagnetic materials are crystalline (Figure 2) and have magnetic ordering temperatures of 330, 338, and 376 K. The latter is the highest yet seen for a molecule-based magnet (Figure 3).

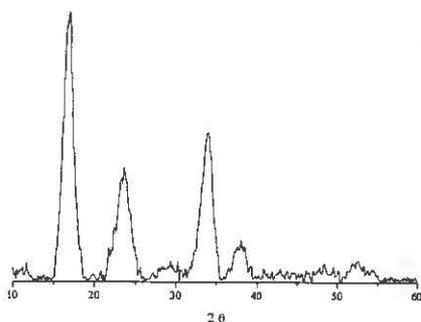


Figure 2.

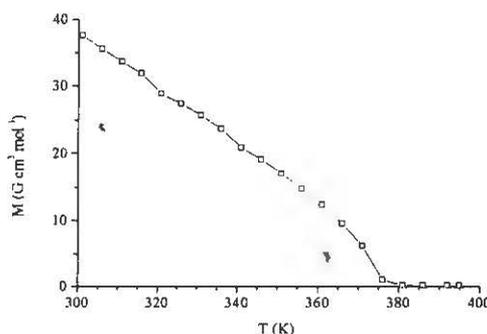


Figure 3

Prussian blues containing  $\text{V}^{\text{III}}$  and  $\text{V}^{\text{IV}}\text{O}$  centers have also been prepared; these include  $\text{V}^{\text{III}}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.67}\cdot 3.2\text{H}_2\text{O}\cdot 0.1\text{MeCN}\cdot 0.2\text{OTs}$  (amorphous,  $T_N = 120$  K), and  $\text{V}^{\text{III}}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.65}\cdot 3.7\text{H}_2\text{O}\cdot 0.06\text{OTs}$  (crystalline,  $T_N = 240$  K),  $\text{V}^{\text{IV}}\text{O}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.65}\cdot 2\text{H}_2\text{O}\cdot 0.5i\text{-PrOH}\cdot 0.1\text{KOTs}$  (crystalline,  $T_N = 85$  K), and  $[\text{NEt}_4]_{0.88}\text{V}^{\text{IV}}\text{O}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.96}\cdot 2\text{H}_2\text{O}\cdot 0.17\text{MeOH}$  (crystalline,  $T_N = 65$  K). The latter are the first examples of Prussian blue analogues constructed from well-defined vanadyl precursors.

The mixed-valent chromium hexacyanochromate  $\text{Cr}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.67}\cdot 2.6\text{H}_2\text{O}$  has been prepared by addition of the tosylate salt  $[\text{Cr}(\text{OH}_2)_6][\text{OTs}]_2$  to  $[\text{NEt}_4]_3[\text{Cr}(\text{CN})_6]$ . This crystalline material is ferrimagnetic with a magnetic ordering temperature of 242 K.

We have investigated the preparation of Prussian blue analogues consisting entirely of  $\text{Cr}^{\text{II}}$  centers. We find that addition of  $\text{Cr}(\text{OTf})_2$  to two equivalents of KCN in  $\text{D}_2\text{O}$  affords  $\text{Cr}^{\text{II}}[\text{Cr}^{\text{II}}(\text{CN})_6]_{0.5}\cdot 2\text{D}_2\text{O}\cdot 0.2\text{KOTf}$  as a crystalline solid. The solid is ferrimagnetic and orders magnetically at 246 K.

Several crystalline cesium-containing  $\text{Cr}^{\text{II}}$  Prussian blues have been made:

$\text{Cs}_2\text{Cr}^{\text{II}}[\text{Cr}^{\text{II}}(\text{CN})_6]\cdot 3\text{H}_2\text{O}\cdot 0.3\text{KOTf}$  ( $T_{\text{N}} = 68$  K),  $\text{Cs}_{0.24}\text{Cr}^{\text{II}}[\text{Cr}^{\text{II}}(\text{CN})_6]_{0.56}\cdot 2.9\text{H}_2\text{O}\cdot 0.05\text{CsOTs}$  ( $T_{\text{N}} = 144$  K), and  $\text{Cs}_{0.96}\text{Cr}^{\text{II}}[\text{Cr}^{\text{II}}(\text{CN})_6]_{0.74}\cdot 2.5\text{H}_2\text{O}\cdot 0.4i\text{-PrOH}$  ( $T_{\text{N}} = 85$  K).

The first manganese(II) hexacyanochromate(II) derivative,  $\text{K}_{1.48}\text{Mn}^{\text{II}}[\text{Cr}^{\text{II}}(\text{CN})_6]\cdot 1.1\text{H}_2\text{O}$ , can be made by addition of  $[\text{Mn}(\text{OH}_2)_5][\text{OTs}]_2$  to aqueous  $\text{Cr}(\text{CN})_6^{4-}$ . This crystalline material is ferrimagnetic and orders magnetically at 87 K. The vanadium(II) derivative  $\text{K}_{2.3}\text{V}^{\text{II}}[\text{Cr}^{\text{II}}(\text{CN})_6]\cdot 3.2\text{H}_2\text{O}\cdot 0.2i\text{-PrOH}\cdot 0.1\text{KOTf}$ , prepared by addition of  $\text{V}(\text{OTf})_2$  to aqueous  $\text{Cr}(\text{CN})_6^{4-}$ , is a poorly crystalline, paramagnetic solid.

Several new Prussian blue analogues have been constructed from the hexacyanovanadate(II) anion and  $\text{Cr}^{\text{II}}$ ,  $\text{Mn}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Co}^{\text{II}}$  cations. Addition of  $\text{Cr}(\text{OTf})_2$ ,  $\text{CsOTf}/\text{Cr}(\text{OTf})_2$ , and  $\text{Mn}(\text{OTf})_2$  to  $\text{K}_4[\text{V}(\text{CN})_6]$  affords the crystalline solids  $\text{Cr}^{\text{II}}[\text{V}^{\text{II}}(\text{CN})_6]_{0.5}\cdot 1.6\text{H}_2\text{O}\cdot 1.4\text{MeCN}\cdot 0.12\text{KOTf}$ ,  $\text{Cs}_{1.48}\text{Cr}^{\text{II}}[\text{V}^{\text{II}}(\text{CN})_6]_{0.87}\cdot 1.4\text{H}_2\text{O}\cdot 0.75\text{MeCN}\cdot 0.12\text{KOTf}$ , and  $\text{K}_{0.88}\text{Mn}^{\text{II}}[\text{V}^{\text{II}}(\text{CN})_6]_{0.72}\cdot 1.6\text{H}_2\text{O}\cdot 0.6\text{MeCN}$ . These ferrimagnetic materials order magnetically at 244, 220, and 160 K, respectively. The  $\text{Cr}^{\text{II}}$  derivatives exhibit compensation behavior and the  $\text{Mn}^{\text{II}}$  compound isomerizes to a material containing  $\text{Mn}^{\text{II}}\text{-CN-V}^{\text{II}}$  linkages that has a magnetic ordering temperature of 137 K. The cobalt(II) and nickel(II) derivatives  $\text{K}_{0.24}\text{Co}^{\text{II}}[\text{V}^{\text{II}}(\text{CN})_6]_{0.56}\cdot 1.1\text{H}_2\text{O}\cdot 1.3\text{MeCN}\cdot 0.11\text{KOTf}$  and  $\text{K}_{0.2}\text{Ni}^{\text{II}}[\text{V}^{\text{II}}(\text{CN})_6]_{0.55}\cdot 1.2\text{H}_2\text{O}\cdot \text{MeCN}$  are crystalline but paramagnetic down to 5 K. Infrared measurements suggest that complete linkage isomerism has occurred, forming  $\text{Co}^{\text{II}}\text{-CN-V}^{\text{II}}$  and  $\text{Ni}^{\text{II}}\text{-CN-V}^{\text{II}}$  linkages.

New magnetic materials constructed from the paramagnetic ion  $\text{Cr}^{\text{I}}(\text{CN})_5\text{NO}^3$  have been prepared. Addition of  $\text{Cr}(\text{OTf})_2$  or  $\text{CsOTf}/\text{Cr}(\text{OTf})_2$  solutions to  $\text{K}_3[\text{Cr}(\text{CN})_5\text{NO}]$  afford solids of stoichiometries  $\text{Cr}^{\text{II}}[\text{Cr}^{\text{I}}(\text{CN})_5\text{NO}]_{0.5}\cdot 2\text{H}_2\text{O}\cdot 1.6\text{MeOH}$  and  $\text{Cs}_{0.5}\text{Cr}^{\text{II}}[\text{Cr}^{\text{I}}(\text{CN})_5\text{NO}]_{0.83}\cdot 1.7\text{H}_2\text{O}\cdot 0.6\text{MeOH}$ . Similar reactions afford the manganese(II) derivatives  $\text{K}_{0.5}\text{Mn}^{\text{II}}[\text{Cr}^{\text{I}}(\text{CN})_5\text{NO}]_{0.83}\cdot 4\text{H}_2\text{O}\cdot 1.5\text{MeOH}$ ,  $\text{Mn}^{\text{II}}[\text{Cr}^{\text{I}}(\text{CN})_5\text{NO}]_{0.68}\cdot 2.2\text{H}_2\text{O}\cdot 1.4\text{MeCN}$ , and  $\text{Cs}_{1.3}\text{Mn}^{\text{II}}[\text{Cr}^{\text{I}}(\text{CN})_5\text{NO}]_{0.86}\cdot 2.2\text{H}_2\text{O}\cdot 0.5\text{MeOH}$ . All of the above compounds are crystalline ferrimagnets with magnetic ordering temperatures of 127, 87, 31, 38, and 32 K, respectively. Addition of  $\text{Co}(\text{OTf})_2$ ,  $\text{Ni}(\text{OTf})_2$ , or  $\text{Cu}(\text{NO}_3)_2$  to  $\text{K}_3[\text{Cr}(\text{CN})_5\text{NO}]$  affords solids with the stoichiometries  $\text{K}_{0.15}\text{Co}^{\text{II}}[\text{Cr}^{\text{I}}(\text{CN})_5\text{NO}]_{0.73}\cdot 0.5\text{H}_2\text{O}\cdot 1.8\text{MeOH}$ ,  $\text{Ni}^{\text{II}}[\text{Cr}^{\text{I}}(\text{CN})_5\text{NO}]_{0.67}\cdot 0.5\text{H}_2\text{O}\cdot 1.8\text{MeOH}$ , and  $\text{Cu}^{\text{II}}[\text{Cr}^{\text{I}}(\text{CN})_5\text{NO}]_{0.67}\cdot 0.25\text{H}_2\text{O}$ . The  $\text{Co}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  compounds are crystalline ferrimagnets ( $T_{\text{N}} = 7$  and 19 K) and the  $\text{Cu}^{\text{II}}$  material is an amorphous and paramagnetic solid.

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