

Molecular-Based Magnets Constructed from Cyanometalate Building Blocks

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Many molecular magnets rely on "through space" interactions to order spins in one or more dimensions; as a consequence, such solids invariably exhibit spontaneous bulk magnetization only at very low temperatures (often well below 30 K).¹⁻³ In order to obtain magnets with higher bulk ordering temperatures, the spin centers must be linked covalently in all three dimensions. For many inorganic solids that can be classified as three-dimensional (3D) polymers, however, it is difficult or impossible to design paramagnetic molecular building blocks that can be polymerized under mild conditions to yield the desired lattice. Thus, the development of molecular magnets with high ordering temperatures depends crucially on the identification of appropriate building blocks that can be used to construct solids with efficient exchange coupling pathways in three dimensions.

Solids related to Prussian blue ($\text{Fe}^{\text{III}}_3[\text{Fe}^{\text{II}}(\text{CN})_6]_2 \cdot x\text{H}_2\text{O}$) are ideal candidates for the preparation of molecular-based magnets: they can be easily prepared at room temperature from well-characterized cyanometalate building blocks, the metal centers are linked covalently into a 3D network, and a wide range of metals with different spin states and oxidation states can be substituted into the lattice.⁴⁻¹³ These features allow control over both the nature and magnitude of the local exchange interaction. Prussian blue is itself ferromagnetic at low temperature, but its rather low magnetic ordering temperature ($T_C = 5.6 \text{ K}$)¹⁵ is a consequence of the diamagnetism of half of the metal centers (the low-spin Fe^{2+} centers, which occupy the strong ligand-field sites). Solids with the Prussian blue structure, but with paramagnetic transition metals in both the M and M' sites, should exhibit ordering temperatures much higher than 5.6 K since the distance between paramagnetic spin carriers is reduced from just over 10 Å (in Prussian blue) to around 5 Å. Analogs of Prussian blue, of the general formula $A_n\text{M}[\text{M}'(\text{CN})_6]_m \cdot x\text{H}_2\text{O}$ (where A is an alkali metal cation), are easily prepared by reaction of hexacyanometalates with transition metal cations. Typically these compounds adopt face-centered cubic (fcc) lattices with linear M'-CN-M-NC-M' bridges along the edge of the unit cell (Figure 1).¹⁴ For $m = 1$, there are two types of octahedral metal sites in the fcc lattice: strong ligand-field sites (M'C₆ coordination environments) and weak ligand-field sites (MN₆ coordination environments). For $m < 1$, the M' sites are fractionally occupied; the M centers surrounding the vacant sites have one (or more) water molecules in their coordination spheres. Zeolitic water molecules and/or charge balancing cations generally occupy the interstitial sites in the face-centered cubic unit cell.

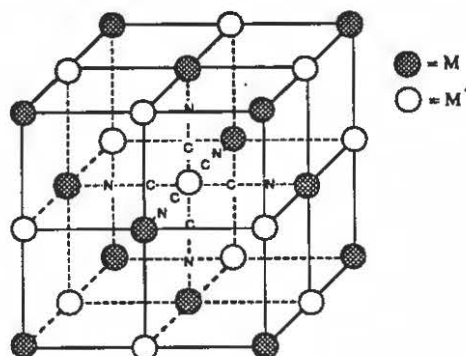


Figure 1. The face-centered cubic unit cell of Prussian blue analogues $A_n\text{M}[\text{M}'(\text{CN})_6]_m \cdot x\text{H}_2\text{O}$.

The nature of the superexchange interactions in Prussian blue analogues is easily understood in terms of the symmetries of the magnetic orbitals present on adjacent metal centers.^{5,8,11} For a Prussian blue structure, magnetic orbitals on adjacent metal centers M and M' will contribute to the superexchange as follows: e_g - e_g and t_{2g} - t_{2g} combinations (if present) have nonzero overlap and give rise to antiferromagnetic contributions; e_g - t_{2g} combinations (if present) have zero overlap and give rise to ferromagnetic contributions. If a metal center contains unpaired electrons in both its e_g and t_{2g} orbitals it will interact with a paramagnetic neighbor to generate both ferromagnetic and antiferromagnetic exchange contributions to the superexchange. The net interaction is simply the sum of the ferromagnetic and

Table I. Structural and magnetic data for new polynuclear cyanometalates.

Compound	a/Å	T _N /K	C ^a	θ/K ^b	Coupling ^c	Ref
(NEt ₄) _{0.4} Mn ^{II} [V ^{II} (CN) ₄ O _{0.5}] _{0.85} ·1.2H ₂ O	NI ^c	230	2.4	160	AF	10,11,13
K _{1.4} Mn ^{II} [V ^{II} (CN) ₆] _{0.85} ·1.3H ₂ O	NI ^c	162	4.3	-23	AF	13
Rb _{1.4} Mn ^{II} [V ^{II} (CN) ₆] _{0.85} ·1.1H ₂ O	10.69	151	3.5	-2.0	AF	13
Cs ₂ Mn ^{II} [V ^{II} (CN) ₆]	10.66	126	11.5	-250	AF	10,11,13
K ₂ Mn ^{II} [Mn ^{II} (CN) ₆]	10.15	41	4.9	-19	AF	9,11
CsNi ^{II} [Mn ^{III} (CN) ₆] ₁ ·H ₂ O	10.42	42	2.96	54	F	11,12
Ni ^{II} ₃ [Mn ^{III} (CN) ₆] ₂ ·12H ₂ O	10.29	30	8.01	42	F	11,12
CsMn ^{II} [Mn ^{III} (CN) ₆] _{1/2} ·H ₂ O	10.69	31	6.2	-32	AF	9,11,12
Mn ^{II} ₃ [Mn ^{III} (CN) ₆] ₂ ·12H ₂ O	10.62	37	16	-39	AF	9,11,12

^a cm³ K mol⁻¹. ^b Negative Weiss constants are characteristic of local antiferromagnetic interactions while positive Weiss constants are characteristic of local ferromagnetic interactions; θ is defined from the equation $\chi = C/(T - \theta)$. ^c Abbreviations used: F = ferromagnetic, AF = antiferromagnetic, NI = Not Indexed.

antiferromagnetic contributions, and for polynuclear cyanometalates the antiferromagnetic contributions dominate.^{5,8,10,11}

Since the magnetic phase transition temperature is directly proportional to the magnitude of the exchange interaction between adjacent spin centers, it should be possible to increase the magnetic ordering temperature in ferrimagnetic Prussian blue analogues by increasing the intrinsic strength of the antiferromagnetic coupling.¹⁶ As the antiferromagnetic exchange interactions in Prussian blue analogues propagate principally through the empty π^* orbitals of the cyanide ligands,^{6,8,10,11} substituting into the structure metals that have high-energy (and more radially expanded) t_{2g} orbitals, viz., early transition metals in lower oxidation states, should increase the magnetic phase transition temperature by increasing the extent of π -backbonding into the cyanide π^* orbitals.

We have utilized this approach to prepare a number of molecular-based magnets related to Prussian blue.⁹⁻¹³ The structural and magnetic data for these polynuclear cyanometalates are reported in Table 1, which is organized from top to bottom according to the metal

present in the strong ligand-field site. The highest magnetic ordering temperatures are observed for those compounds which contain low-valent vanadium centers substituted into the strong ligand-field sites.^{10,11} One such compound, $\text{Rb}_{1.4}\text{Mn}^{\text{II}}[\text{V}^{\text{II}}(\text{CN})_6] \cdot 1.1\text{H}_2\text{O}$, is particularly interesting; a comparison of the magnetic ordering temperature of $\text{Rb}_{1.4}\text{Mn}^{\text{II}}[\text{V}^{\text{II}}(\text{CN})_6]_{0.85} \cdot 1.1\text{H}_2\text{O}$ with those of $\text{CsMn}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot \text{H}_2\text{O}$ ⁶ and $\text{Mn}^{\text{II}}[\text{Mn}^{\text{IV}}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ ⁵ illustrates the extent to which the magnetic ordering temperature is enhanced by substitution of low-valent vanadium centers into the strong ligand-field sites. All three compounds have d^5 Mn^{II} centers in the weak ligand-field sites and d^3 metal centers in the strong ligand-field sites; the principal difference is that the energies of the t_{2g} orbitals in the latter sites decrease as the metal changes from V^{II} to Cr^{III} to Mn^{IV} . The relative magnetic ordering temperatures of 130, 90, and 49 K for $\text{Rb}_{1.4}\text{Mn}^{\text{II}}[\text{V}^{\text{II}}(\text{CN})_6]_{0.85} \cdot 1.1\text{H}_2\text{O}$, $\text{CsMn}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot \text{H}_2\text{O}$, and $\text{Mn}^{\text{II}}[\text{Mn}^{\text{IV}}(\text{CN})_6] \cdot x\text{H}_2\text{O}$, respectively, clearly show that substitution of transition metals with higher energy (and more radially expanded) t_{2g} orbitals into the strong ligand-field sites leads to higher magnetic phase transition temperatures. As the back-bonding with the cyanide π^* orbitals becomes more effective, the coupling between the adjacent spin centers increases.^{10,11}

A second example of a vanadium-based polynuclear cyanometalate is the compound $(\text{NEt}_4)_{0.4}\text{Mn}^{\text{II}}[\text{V}^{\text{II}}(\text{CN})_4\text{O}_{0.5}]_{0.8} \cdot 1.2\text{H}_2\text{O}$, which is prepared by treatment of $(\text{NEt}_4)_4[\text{V}(\text{CN})_6]$ with $\text{Mn}(\text{OSO}_2\text{CF}_3)_2(\text{CH}_3\text{CN})_2$.^{10,11} The ferrimagnetic phase transition temperature of 230 K, as shown in Figure 2, is among the highest reported for any molecular-based magnetic material. Only two other molecular magnets exhibit higher magnetic ordering temperatures: Miller's $\text{V}(\text{tcne})_2 \cdot x\text{CH}_2\text{Cl}_2$ compound (T_N estimated to be ~ 400 K),¹⁷ and Verdaguer's cyanochromate $[\text{Cr}_5(\text{CN})_{12}] \cdot 10\text{H}_2\text{O}$ ($T_N = 240$ K).⁸

The powder X-ray diffraction pattern of $(\text{NEt}_4)_{0.4}\text{Mn}^{\text{II}}[\text{V}^{\text{II}}(\text{CN})_4\text{O}_{0.5}]_{0.8} \cdot 1.2\text{H}_2\text{O}$ clearly shows that the sample is polycrystalline but that it does not adopt a *fcc* lattice. The non-cubic powder diffraction pattern and the 4:1 cyanide-to-vanadium ratio both suggest that the structure of $(\text{NEt}_4)_{0.4}\text{Mn}^{\text{II}}[\text{V}^{\text{II}}(\text{CN})_4\text{O}_{0.5}]_{0.8} \cdot 1.2\text{H}_2\text{O}$ is more complex than that of its *fcc* analogue $\text{Rb}_{1.4}\text{Mn}^{\text{II}}[\text{V}^{\text{II}}(\text{CN})_6]_{0.85} \cdot 1.1\text{H}_2\text{O}$.

The orbital model invoked to explain the superexchange interactions affords insights that allow us to prepare magnetically ordered solids with specifically tailored magnetic exchange interactions.

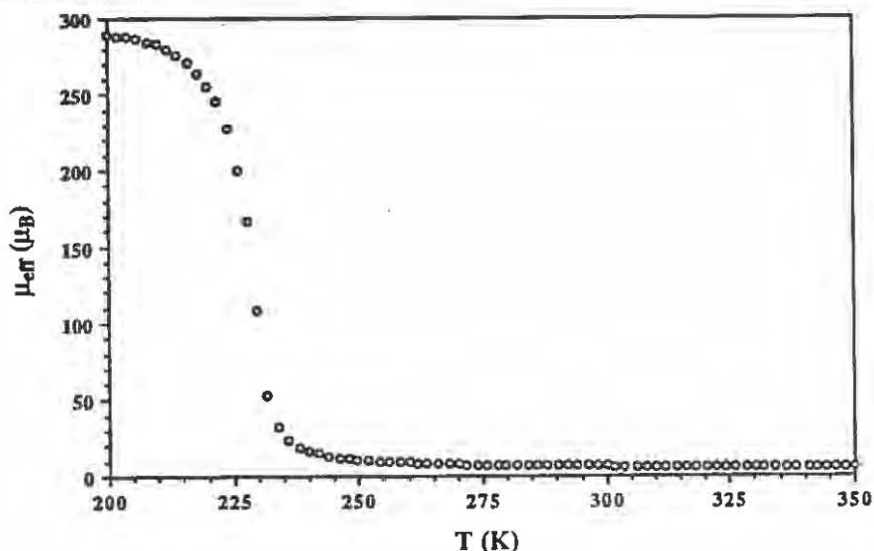


Figure 2. Temperature dependence of μ_{eff} for $(\text{NEt}_4)_{0.4}\text{Mn}^{\text{II}}[\text{V}^{\text{II}}(\text{CN})_4\text{O}_{0.5}]_{0.8} \cdot 1.2\text{H}_2\text{O}$ in an applied magnetic field of 50 G. The sharp rise in μ_{eff} at 230 K indicates the onset of long-

For example, ferromagnets can be prepared by addition of nickel(II) salts ($t_{2g}^6e_g^2$) to low-spin cyanometalates with fewer than six d-electrons.^{7,11,12} The compound $Ni^{II}_3[Mn^{III}(CN)_6]_2 \cdot 12H_2O$, prepared by addition of Ni^{2+} to $[Mn(CN)_6]^{3-}$ ($t_{2g}^4e_g^0$), is such a ferromagnet. Low field magnetization measurements show that the magnetic ordering temperature is 30 K. The stoichiometry of this material requires that vacancies be present in the lattice: only 2/3 of the M' sites are occupied.

Since the magnetic phase transition temperature is also proportional to the number of nearest neighbors, it should be possible to increase the magnetic phase transition temperature in $Ni^{II}_3[Mn^{III}(CN)_6]_2 \cdot 12H_2O$ by filling the vacancies in the three-dimensional bridging framework.¹⁸ By carrying out the reaction of Ni^{II} and $[Mn^{III}(CN)_6]^{3-}$ in the presence of a cesium salt, the 1:1 product $CsNi^{II}[Mn^{III}(CN)_6] \cdot H_2O$ is obtained; in this material, all the metal lattice sites are occupied.^{11,12} Variable temperature magnetic measurements reveal that $CsNi^{II}[Mn^{III}(CN)_6] \cdot H_2O$ orders magnetically at 42K, a 12 K increase relative to $Ni^{II}_3[Mn^{III}(CN)_6]_2 \cdot 12H_2O$. This increase illustrates the benefits of a vacancy-free framework in these polynuclear cyanometalates.

The preparation of inorganic solids from hexacyanometalate molecular building blocks has led to a general route for the preparation of materials with high magnetic ordering temperatures. Through the appropriate choice of molecular building blocks (i.e., by considering the symmetry properties of the magnetic orbitals on the adjacent spin carriers), solids that exhibit ferromagnetic or ferrimagnetic behavior can be prepared. While site vacancies lead to reductions in the magnetic ordering temperature, large increases in T_N can be achieved by substituting into the lattice metals that backbond strongly into the cyanide π^* orbitals (i.e., early transition metals in low oxidation states). An understanding of the electronic and structural factors that favor strong coupling between adjacent spin carriers has led to the preparation of molecular-based magnetic materials with magnetic phase transition temperatures over 200 K. Clearly, remarkable progress is being made toward the preparation of a room temperature molecular-based magnet and further improvements in T_N can be expected in the near future.

References

1. Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 385-415.
2. Kahn, O. *Molecular Magnetism*; VCH Publishers, Inc.: New York, 1993.
3. *Magnetic Molecular Materials*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; NATO ASI Series E, Vol. 198; Plenum: New York, 1991.
4. Bozorth, R. M.; Williams, H. J.; Walsh, D. E. *Phys. Rev.* **1956**, *103*, 572-578.
5. Klenze, R.; Kanellakopulos, B.; Trageser, G.; Eysel, H. H. *J. Chem. Phys.* **1980**, *72*, 5819-5828.
6. Babel, D. *Comments Inorg. Chem.* **1986**, *5*, 285-320.
7. Gadet, V.; Mallah, T.; Castro, I.; Verdaguer, M. *J. Am. Chem. Soc.* **1992**, *114*, 9213-9214.

8. Mallah, T.; Thiébaud, M.; Verdaguer, M.; Veillet, P. *Science* **1993**, *262*, 1554-1557.
9. Entley, W. R.; Girolami, G. S. *Inorg. Chem.* **1994**, *33*, 5165-5166.
10. Entley, W. R.; Girolami, G. S. *Science* **1995**, *268*, 397-400.
11. Entley, W. R.; Treadway, C. R.; Girolami, G. S. *Molecular Crystals and Liquid Crystals, Proceedings of the 4th International Conference on Molecule-Based Magnets, 16-21 October 1994, Salt Lake City*, Gordon and Breach: Yverdon-les-Bains, Switzerland, in press.
12. Entley, W. R.; Treadway, C. R.; Girolami, G. S. *Inorg. Chem.*, in preparation.
13. Entley, W. R.; Girolami, G. S. *J. Am. Chem. Soc.*, in preparation.
14. Ludi, A.; Güdel, H. U. *Struct. Bonding (Berlin)* **1973**, *14*, 1-21.
15. Herren, F.; Fischer, P.; Lüdi, A.; Hälg, W. *Inorg. Chem.* **1980**, *19*, 956-959.
16. Néel, L. *Ann. Phys. (Paris)* **1948**, *3*, 137-198.
17. Manriquez, J. M.; Yee, G. T.; Mclean, R. S.; Epstein, A. J.; Miller, J. S. *Science* **1991**, *252*, 1415-1417.
18. Kittel, C. *Introduction to Solid State Physics, 6th Ed.*; Wiley: New York, 1986; Chapter 15.