

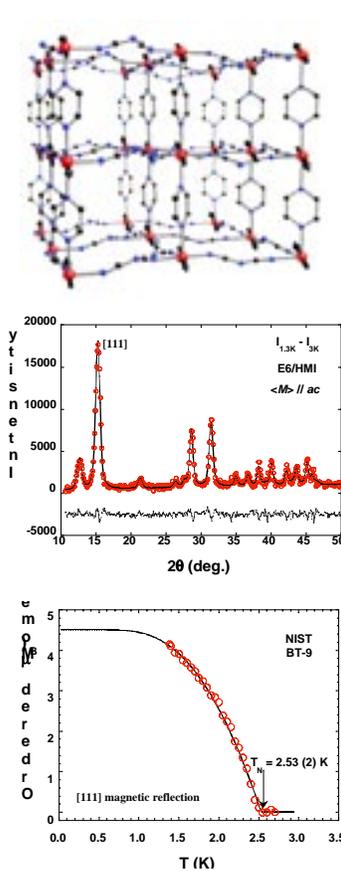
Magnetic Ordering and Spin Excitations in $\text{Mn(dca)}_2(\text{pyz})$ { $\text{dca} = \text{N}(\text{CN})_2^-$; $\text{pyz} = \text{pyrazine}$ }

J. L. Manson^{1*}, H. N. Bordallo², L. C. Chapon¹, J. C. Cook³, J. R. D. Copley³,
J. W. Lynn³, R. Feyerherm⁴, A. Loose⁴ and D. N. Argyriou¹

¹Materials Science Division and ²Intense Pulsed Neutron Source, Argonne National Laboratory, Argonne, IL 60439

³NIST Center for Neutron Research, Gaithersburg, MD 20899

⁴Hahn-Meitner Institut, BENSC, Berlin, Germany 14109



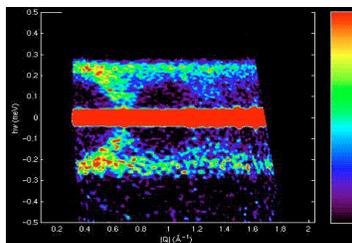
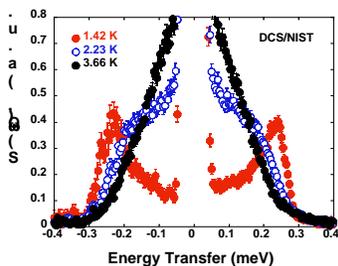
Upper panel: Redefined zero-field magnetic structure of $\text{Mn(dca)}_2(\text{pyz})$ based on statistically improved data taken on E6 at HMI.

Middle panel: Rietveld fit of the E6 NPD data indicates a collinear spin orientation parallel to the ac -diagonal. We believe this behavior arises from a competition between dipolar exchange and single-ion anisotropy.

Lower panel: Temperature variation of the ordered magnetic moment. At 1.35 K, $\langle M \rangle = 4.15(6) \mu_B$ which is reduced from the expected value of $5 \mu_B$. This moment reduction is not unusual and is attributed to covalency effects. The solid line is a fit to the Brillouin function. A power law fit yielded $\beta = 0.38$ which is in good agreement with a 3D Heisenberg AFM.

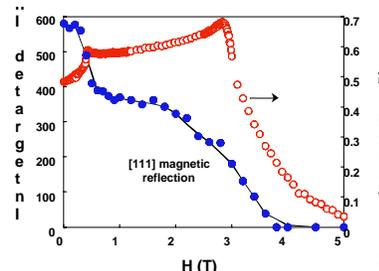
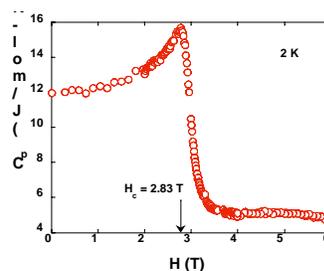
Molecular magnetism is an area of increasing interdisciplinary interest. Magnetic solids based on the dicyanamide ion, $[\text{N}(\text{CN})_2]^-$, abbreviated (dca), such as M(dca)_2 [$\text{M} = \text{V, Cr, Mn, Fe, Co, Ni}$], have shown interesting bulk magnetic behavior.[1-3] Mn(dca)_2 is comprised of high-spin $S = 5/2 \text{ Mn}^{2+}$ ions that are arranged on a rutile-like crystal lattice. A canted AFM state sets in below 16 K while the Ni-analog is a FM below 21 K.

Alteration of the crystal lattice can be achieved by introducing auxiliary organic bridging ligands. $\text{Mn(dca)}_2(\text{pyz})$ is such an example and contains 2D Mn(dca)_2 arrays that are held together by pyz ligands to yield a ReO_3 -like 3D network structure.[4] The long organic spacer ligands promote formation of two interwoven lattices. The ensuing magnetic properties are expectedly very different from those of parent Mn(dca)_2 . Using several neutron scattering techniques, we have revealed the origin of long-range magnetic ordering and spin excitations in this complex solid.



Upper panel: Temperature-dependence of the spin wave excitation in $\text{Mn(dca)}_2(\text{pyz})$ measured on a powder sample using the new DCS at NIST.

Lower panel: Q-variation of the spin wave dispersion acquired at 1.42 K on DCS. Because we are measuring a powder sample, only the first Brillouin zone is clearly visible. With the advent of cold neutron INS instruments, much information can be learned from powder samples.



Upper panel: Field-dependent specific heat for $\text{Mn(dca)}_2(\text{pyz})$ taken on a pressed pellet at 2 K. The anomaly occurring near 2.83 T is thought to arise from a field-induced spin flop to paramagnetic phase transition, H_c . The spin flop transition, H_{sf} , occurs at a lower field but was not detected by this technique since it involves a spin state equilibrium.

Lower panel: The [111] magnetic reflection decreases to 2/3 its value at the spin flop transition. A broad plateau region between 0.5 and 4 T was observed which coincides with a highly fluctuating paramagnetic state. Above 4 T, a fully aligned ferromagnetic state is achieved. The $\chi(H)$ data depicts two magnetic phase transitions at 0.43 and 2.83 T, which are assigned to spin flop and paramagnetic phase transitions, respectively.

With our knowledge of H_{sf} , H_c and eqs. 1 and 2, we can calculate the exchange field, H_E , and anisotropy field, H_A , for $\text{Mn(dca)}_2(\text{pyz})$:

$$H_{sf} = \sqrt{2H_E H_A - H_A^2} \quad (1)$$

$$H_c = 2H_E - H_A \quad (2)$$

$$H_A = 0.065 \text{ T and } H_E = 1.45 \text{ T}$$

$$\frac{H_A}{H_E} = 0.045 \quad \text{Similar to MnF}_2$$

Larger than that observed for Mn(dca)_2 (0.001)