Prussian Blue Materials

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Anomalous Stoichiometry, Layered Structure, and Magnetic Ordering for the Prussian Blue Analogue $[NEt_4]_2[Mn^{II}{}_3(CN)_8]$**

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Magnetic ordering has been reported for several mixed-metal hexacyanometalates possessing the Prussian blue structural motif. These materials magnetically order with critical temperatures, T_c, as high as approximately 100 °C.[1–3] They possess a) a face centered cubic (fcc) unit cell ($a \approx 10.5$ Å), b) C-bound to M $[M(CN)_6]^{n-}$ surrounded by M′ that is typically bound to six cyanide nitrogens, and c) linear -M′-N≡C-M-C≡N-M′- linkages. While structurally related, Prussian blues can have several compositions, for example, $M'^{III}{}_4[M^{II}(CN)_6]_3$, and $C^+{}_2M'^{II}[M^{II}(CN)_6]$, that are typically hydrated. The canonical cell contains significant void space that can accommodate cations and/or solvent, and in some cases, a fraction of the cyanides are missing. $K_2Mn^{II}[Mn^{II}(CN)_6]$, however, has a distorted lattice with nonlinear -M′-N≡C linkages with an average ∡ M′-N≡C of 147°.[4] The relatively high observed T_c values are due to the strong superexchange[5] between adjacent metal sites through the bridging cyanide. To study the effect of cation size in Prussian blue related magnets, and make new magnetic materials, we investigated the use of the significantly larger NEt_4^+ and targeted $[NEt_4]_2Mn^{II}[Mn^{II}(CN)_6]$, as a reaction product from Mn^{II} salts with $[NEt_4]CN$. Herein, we report the unexpected layered structure of $[NEt_4]_2[Mn_3(CN)_8]$ stoichiometry, and its magnetic ordering.

The reaction of $[NEt_4]CN$ and $Mn(O_2CMe)_2$ formed a green precipitate, **1**.[6] The structure of **1** was solved by real space simulated annealing and Rietveld refinement of the synchrotron powder diffraction data (Figure 1).[7,8] The composition of **1** was not known prior to the powder X-ray diffraction measurements; it was determined only when the structure was solved and refined.[9] **1** has a trigonal unit cell [$P\bar{3}m1$, $a = 7.9992(3)$ Å, $c = 14.014(1)$ Å]; hence, it does not exhibit a face-centered cubic lattice that is typical of Prussian blue.[10,11]

The structure of **1** has two distinct Mn^{II} ions in a 1:2 ratio; one octahedrally and two tetrahedrally coordinated.[12] Due to the similarity of C and N they cannot be distinguished from X-ray diffraction alone. Nonetheless, due to the propensity of cyanide to bind to a metal center via carbon, the octahedral site has six C-bound cyanides with a 1.92(6) Å Mn–C bond distance (Figure 2a). This is in accord with the average Mn–CN bonds of 1.95 Å reported for $Na_4[Mn(CN)_6]\cdot 10H_2O$,[13a,b] and for $K_2Mn[Mn(CN)_6]$,[4] but is significantly shorter than the 2.22 Å Mn–NC bonds observed for $[Mn(NCMe)_6][MnI_4]$,[14] 2.24 Å for $K_2Mn[Mn(CN)_6]$,[4] 2.207 Å for $NaMn[Cr(CN)_6]$,[10] and 2.184 Å for $Mn_3[Co(CN)_6]_2\cdot 12H_2O$.[13c] Due to the bonding with six strong-field CN^- carbons, this Mn^{II} ion is expected to be low-spin and Jahn–Teller distorted, with ca. 0.1 Å differences in the Mn–C distances, but due to the trigonal symmetry, all Mn–CN distances must be crystallographically equal, and the Jahn–Teller distortion axis is evidently random or fluctuating. Magnetic measurements (see below) confirm the low-spin assignment of the octahedral Mn^{II}. The ∡ Mn-C≡N is 176(2)° in accord for $K_2Mn[Mn(CN)_6]$ (174.5°) and $Na_4[Mn(CN)_6]\cdot 10H_2O$ (177°).[13a,b]

The other Mn^{II} binds to four cyanides—three bridging, and one terminal. The bridging cyanides are N-bound with 2.19(2) Å Mn–N distances to three different octahedral MnC_6 sites (Figure 2b) in accord with the Mn–N distances discussed above. The fourth, terminal cyanide does not bridge to another Mn^{II}, and presumably is C-bound to the tetrahedral Mn^{II} site with Mn–C = 2.01(21) Å that is in accord with the Mn–C distances discussed above. The ∡ Mn-N≡C is 166(2)° and is intermediate between typical Prussian blue structured

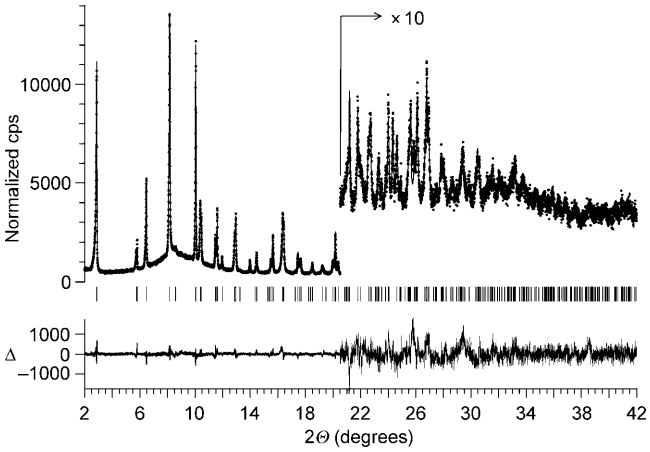

Figure 1. High-resolution synchrotron powder diffraction data (dots) and Rietveld fit of the data for **1**, with disordered cation (top; cps = counts per second). The lower traces for each plot are the differences Δ (measured minus calculated) plotted to the same vertical scale.

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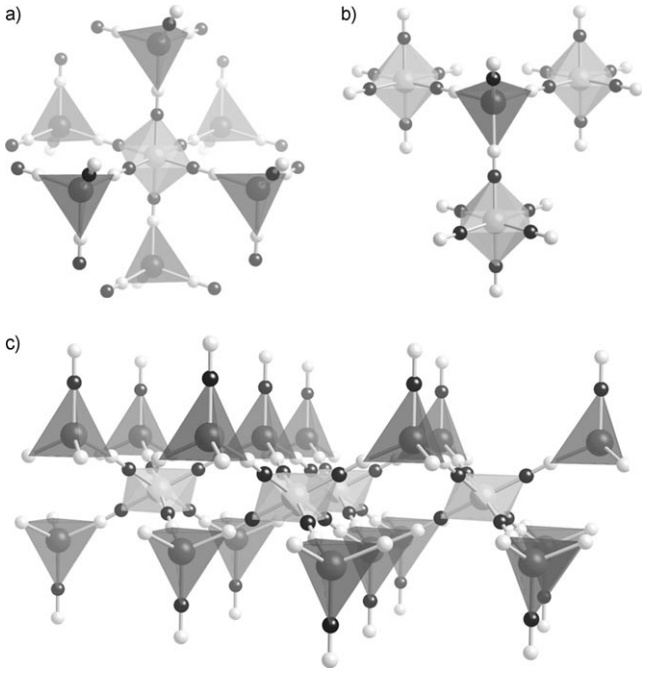

Figure 2. a) Six tetrahedral $[Mn^{II}(CN)_4]^{2-}$ ions surrounding each $[Mn^{II}(CN)_6]^{4-}$ octahedron; b) three octahedral $[Mn^{II}(CN)_6]^{4-}$ ions surrounding each $[Mn^{II}(CN)_4]^{2-}$ tetrahedron; c) perspective view of the 2-D network lattice for $[NEt_4]_2[Mn^{II}_3(CN)_8]$. The disordered cations and water are not depicted.

materials (180°), and the anomalous 147.1° average reported for $K_2Mn[Mn(CN)_6]$.[4] The $[Mn_3(CN)_8]^{2-}$ layers are separated by 14.014 Å (c) with no covalent interlayer bonding.

The 5 to 300 K magnetic susceptibility, $\chi(T)$, was determined on a Quantum Design MPMS-5XL magnetometer, and the 300 K χT-value of 9.20 emu K mol^{-1} is in accord with the expected spin-only value of 9.125 emu K mol^{-1} for one low-spin Mn^{II} and two high-spin Mn^{II} ions for $[NEt_4]_2Mn_3(CN)_8$. $\chi T(T)$ decreases gradually with decreasing temperature until reaching a minimum at 215 K before increasing to 50 K, when it rises sharply reaching a value of 360 emu K mol^{-1} at 22 K (Figure 3). The minimum arises from antiferromagnetic coupling and the peak in $\chi T(T)$ suggests magnetic ordering. The $\chi^{-1}(T)$ data can be fit to the Curie–Weiss expression, $\chi \propto (T-\theta)^{-1}$, above 175 K with $\theta = 32$ K indicative of effective short-range ferromagnetic coupling (Figure 3).

The 10 Oe zero field cooled (ZFC) and field cooled (FC) magnetizations, $M(T)$, show a bifurcation point (T_b) at 25 K. A T_c of 27 K is obtained from an extrapolation of the low-field $M(T)$ data to the temperature at which $M(T) \rightarrow 0$.

The 5 K field-dependent magnetization, $M(H)$, rapidly increases up to 2.5 kOe and approaches saturation at 49800 emu Oe mol^{-1} at 9 T, but it is still increasing with increasing applied field (Figure 4). This is in accord with 50265 emu Oe mol^{-1} expected for ferrimagnetic behavior arising from antiferromagnetic coupling between the $S = 1/2$ octahedral Mn^{II} site and the two $S = 5/2$ tetrahedral Mn^{II} sites. **1** shows a coercive field of 1140 Oe, and remnant magnetization of 22800 emu Oe mol^{-1} at 5 K, respectively, suggesting that it is a hard ferrimagnet.[4]

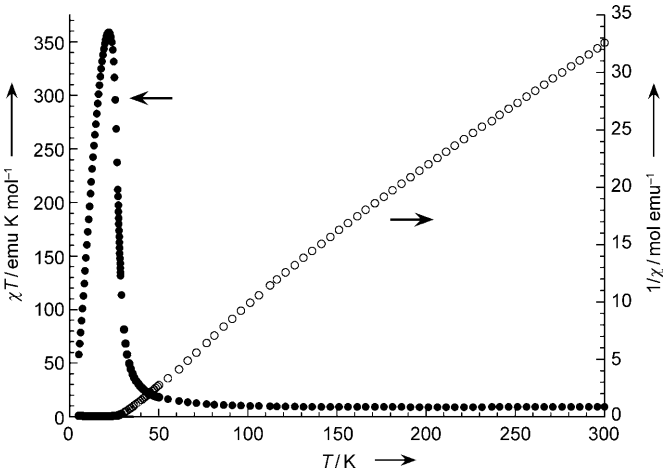

Figure 3. $\chi T(T)$ (●) and $1/\chi(T)$ (○) for $[NEt_4]_2[Mn^{II}_3(CN)_8]\cdot 1/2\,H_2O$ in a 1 kOe applied field.

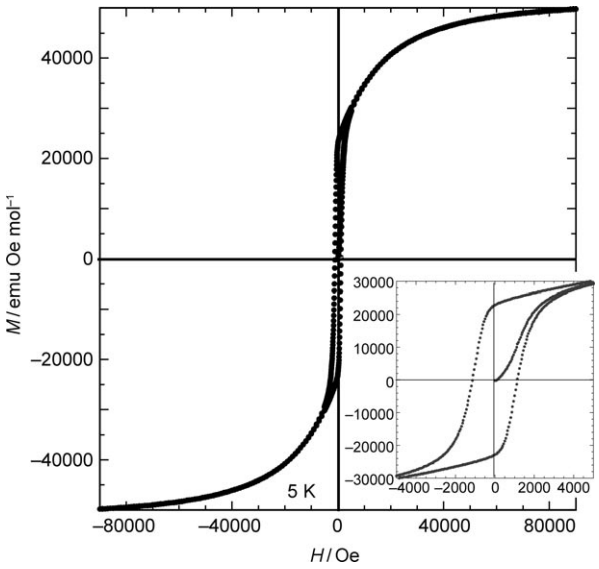

Figure 4. 5 K $M(H)$ showing hysteretic behavior for $[NEt_4]_2[Mn^{II}_3(CN)_8]\cdot 1/2\,H_2O$.

The $\chi'(T)$ and $\chi''(T)$ components of ac susceptibility are also characteristic of ferromagnetic ordering (Figure 5). Both $\chi'(T)$ and $\chi''(T)$ are frequency independent. The maximum in the 33 Hz $\chi'(T)$ data occurs at T_c of 25 K in accord with the T_b.

The breadth of Prussian blue analogues has been expanded with the discovery of the unprecedented $[NEt_4]_2[Mn_3(CN)_8]$ stoichiometry and its layered (2-D) structure. It possesses low-spin $[Mn^{II}(CN)_6]^{4-}$ ions typical of Prussian blue analogues, but each N binds to high-spin tetrahedral Mn^{II} centers, not the expected octahedral Mn^{II} centers, as occurs for $K_2Mn^{II}[Mn^{II}(CN)_6]$.[4] The low-spin octahedral Mn^{II} antiferromagnetically couples to the two high-spin tetrahedral Mn^{II} leading to a ferrimagnet with $T_c = 25$ K, with a higher than expected coercive field and remnant magnetization of 1140 Oe and 22800 emu Oe mol^{-1}, respectively.

CCDC 767545 contains the supplementary crystallographic data for this paper. These data can be obtained free

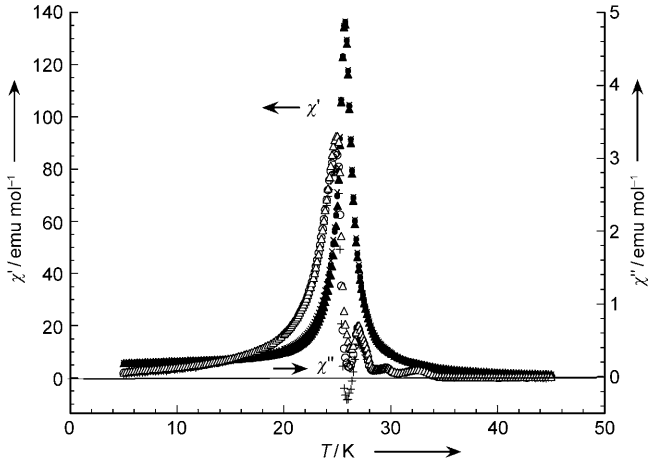

Figure 5. $\chi'(T)$ and $\chi''(T)$ for $[NEt_4]_2[Mn^{II}{}_3(CN)_8]\cdot 1/2\,H_2O$ at 33 (×, +), 100 (●, ○), and 1000 Hz (▲, △).

of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[6] Dropwise addition of an aqueous 3 mL solution of NEt_4CN (575 mg, 3.68 mmol) into a vigorously stirred 2 mL aqueous solution of $Mn(O_2CCH_3)_2$ (210 mg, 1.21 mmol) ensuring that the drops land at the center of the vortex initially led to a yellow precipitate that turned light-green within 10 min. After stirring for 3 h the light-green product was collected by filtration, washed with H_2O (2 × 10 mL), MeOH (2 × 10 mL), and Et_2O (2 × 10 mL). The product was dried under vacuum for 3 h (yield: 233 mg, 91 %). IR (KBr; $\tilde{\nu}$ in cm^{-1}): OH 3630 (vw); CH 3016 (w), 2992 (w), 2952 (w); CN 2081 (s, sh), 2062 (s); 1463 (m), 1404 (m), 1308 (vw), 1186 (m), 1080 (w), 1037 (m) 1008 (m), 793 (m), 466 (m). Calcd for $[NEt_4]_2[Mn^{II}{}_3(CN)_8]\cdot x\,H_2O$ ($x = 0.25$), $C_{24}H_{40.5}Mn_3N_{10}O_{0.25}$: C 45.18, H 6.40, N 21.96; found C 45.14, H 6.55, N 21.83. TGA was also used to determine x, which varied from sample to sample, and it was 0.5 for the sample whose magnetic properties are reported herein.

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[8] $[NEt_4]_2[Mn^{II}{}_3(CN)_8]$: $P\bar{3}m1$, $a = 7.9992(3)$ Å, $c = 14.014(1)$ Å; $V = 776.6(1)$ Å^3; $T = 295$ K; $Z = 1$; $Rwp = 6.58\,\%$; $\chi^2 = 2.15$.

[9] NEt_4^+ and H_2O were disordered in the lattice. The refinements were performed with several pseudo-atoms within the voids. We believe that this procedure does not degrade the validity of the Mn: CN framework structure reported herein. The cations can be visualized by maximum entropy maps: J.-H. Her, Ph.D thesis, Department of Physics & Astronomy, Stony Brook University, Stony Brook, NY (2007). The disordered solvent does lead to unusually large error bars for the position of the terminal cyanide relative to the tetrahedral Mn site.

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