Anomalous Non-Prussian Blue Structures and Magnetic Ordering of K$_2$Mn$^{II}$[Mn$^{II}$](CN)$_6$ and Rb$_2$Mn$^{II}$[Mn$^{II}$](CN)$_6$

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The reaction of Mn$^{II}$ and KCN in aqueous and non-aqueous media leads to the isolation of three-dimensional (3-D) Prussian blue analogues, K$_2$Mn[Mn(CN)$_6$]$_3$ (1a–d, 1e, respectively). Use of Rb$_2$CN forms Rb$_2$Mn[Mn(CN)$_6$]$_3$ (2). 1 and 2 are isomorphous, monoclinic, $P2_1/n$. 1 [α = 10.1786(1) Å, β = 7.4142(1) Å, c = 6.9758(1) Å, β = 90.206(1)$^\circ$]; 2 [α = 10.4101(1) Å, β = 7.4492(1) Å, c = 7.2132(1) Å, β = 90.072(1)$^\circ$], with a small monoclinic distortion from the face centered cubic (fcc) structure that is typical of Prussian blue structured materials that was previously reported for K$_2$Mn[Mn(CN)$_6$]. Most notably the average Mn--N--C angles are 148.8$^\circ$ and 153.3$^\circ$ for 1 and 2, respectively, which are significantly reduced from linearity. This is attributed to the ion-ionic nature of high spin Mn$^{II}$ accommodating a reduced M–CN–M angle and minimizing void space. Compounds 1a,b have a sharp, strong ν$_{OH}$ band at 3628 cm$^{-1}$, while 1e lacks a ν$_{OH}$ absorption. The ν$_{OH}$ absorption in 1a,b is attributed to surface water, as use of D$_2$O shifts the ν$_{OH}$ absorption to 2677 cm$^{-1}$, and that 1a–e are isostructural. Also, fcc Prussian blue-structured Cs$_2$Mn[Mn(CN)$_6$]$_3$ (3) has been structurally (Fm$\overline{3}$m; a = 10.6061 Å) and magnetically characterized. The magnetic ordering temperature, $T_c$, increases as K$^+$(41 K) > Rb$^+(34.6 K) >$ Cs$^+(21 K)$ for A$_2$Mn[Mn(CN)$_6$]$_3$ in accord with the increasing deviation for linearity of the Mn–N–C angle [148.8$^\circ$(K) > 153.3$^\circ$(Rb) > 180$^\circ$(Cs)], decreasing size of the cation (increasing electrostatic interactions). Hence, the bent cyanide bridges play a crucial role in the superexchange mechanism by increasing the coupling via shorter Mn(II)···Mn(II) separations, and perhaps enhanced overlap. In addition, the temperature dependent magnetic behavior of K$_2$Mn[Mn(CN)$_6$]$_3$·3H$_2$O is reported.

Introduction

Ferri- and to a lesser extent ferromagnetic ordering has been reported for several hexacyanometalates possessing the Prussian blue structure.$^{1–3}$ Critical temperatures, $T_c$, as great as ~100 °C have been reported for KV$^{II}$[Cr$^{III}$](CN)$_6$$_2$H$_2$O−0.1(KO$_3$SCF$_3$)$_{3a}$ and KV$^{II}$[V$^{III}$][V$^{III}$](CN)$_6$(SO$_4$)$_{0.058}$[V$^{III}$](CN)$_6$$_{0.79}$(SCF$_3$)$_{0.43}$ with the anticipation that they may find applications in areas such as magnetic shielding and spintronic memory storage devices.$^4$ Magnetic ordering occurs in these materials because of the strong spin coupling between adjacent metal sites via the superexchange interaction of the cyanide ligand. This family includes Mn$^{II}$[Mn$^{II}$](CN)$_6$(T$_c$ = 31 K), Mn$^{III}$[Mn$^{II}$](CN)$_6$$_2$·2H$_2$O

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(12 ≤ z ≤ 16; Te = 35.5 K),8,9 CsMnHl[MnIII(CN)6]·1/2(H2O) (Tc = 31 K),8 and MnHl[MnIV(CN)6]·1.14H2O (Te = 49 K).10 In the case of MnHl[MnII(CN)6]·12H2O, the C-bonded low spin (ls) MnII (ls 3, S = 1) interacts with the N-bond high spin (hs) MnII (hs 3, S = 5/2) ferromagnetically.8,9 Additionally, face-centered cubic (fcc) K3MnII, [MnII(CN)6]8,11,12 and NaNan[Mn(CN)6]13 were reported to be ferromagnets with Tc of 41 and 60 K, respectively.

Recently, Ml[MnII(CN)6] (M = Co, Ni) and MnII[MnII-CN(CN)6] (M = V, Cr, Mn) made in non-aqueous media showed unexpected magnetic behaviors.15,16 The formation of the water-free lattice led to spin-glass behavior that is typical of Prussian blue analogues (PBAs).1–3 Also, the study of anhydrous Fe[Mn(CN)6] and its hydrate revealed that they have uncommon mixed valency and magnetic properties.13

Keggin and Miles originally reported the structure of A3Fe[Fe(CN)6] (A = alkali cation) as being fcc, and this has been recognized as the general structure for A3M[MIV-CN(CN)6]·2H2O PBAs.14 PBAs have two distinct metal sites consisting of C bonded to strong field metal sites, M'C6, and N bonded to weak field metal sites, M'N6, and charge balancing cations and/or water molecules are located within the void spaces of each lattice. Often PBAs have incomplete lattices with water coordinated to M rather than nitrogen.15,16

Herein, we investigate the magnetic properties of K2MnII, [MnII(CN)6] (1a–e) and Rb,MnII[MnII(CN)6] (2), and report the first non-face centered cubic structure of A2MnII[MnII-CN(CN)6] (A = K, Rb) composition with bent Mn-CN-Mn linkages. For comparison the magnetic behavior of K2MnII [Hl(CN)6] is revisited.17 We also extend the fcc Prussian blue structure type with the preparation and structural and magnetic characterization of Cs3MnII[MnIII(CN)6] (3). The genesis of this study was to identify a route to make [NEt4][MnII(CN)6], and these results will be reported later.19

Experimental Section

KCN, MnO2·CMC2·4H2O, and MnCl2·4H2O were used as purchased. MnO2·CMC2·4H2O was dehydrated by heating in a vacuum oven at 100 °C over P2O5 for 24 h, and after putting MnO2·CMC2·4H2O into the DryBox, x was determined to be 2 from a thermogravimetric analysis (TGA). RbCN was obtained as a gift from M. C. DeLong, and used as received.20 K₄[Mn(CN)₆]21a and CsCN21b were prepared via literature routes. Diethyl ether was purified through an activated alumina dual-column purification system under a positive pressure of N2, while H2O was purified through a Barnstead “E-pure” water purification system and deoxygenated through distillation under N2. All other solvents were distilled from the appropriate drying agents under nitrogen before use. All syntheses were performed in an oxygen-free (<1.0 ppm O2) wet or drybox.

Physical Methods. Infrared spectra were recorded from 400 to 4000 cm⁻¹ as KBr pellets. Thermogravimetric analyses were performed at a scan rate of 5 °C/min using a TGA 2050 TA Instruments located in a Vacuum Atmospheres DriLab under nitrogen to protect air- and moisture-sensitive samples. Samples were placed in an aluminum pan and heated at 5 °C/min under a continuous 10 mL/min nitrogen flow. Elemental analyses were performed by GCL & Chemisar Laboratories.

Magnetic susceptibilities were measured in 1000 (1a–d and 2) and 500 Oe (1e and 3) applied fields between 5 and 300 K on a Quantum Design PPMS superconducting quantum interference device (SQUID) equipped with a reciprocating sample measurement system, low field option, and continuous low temperature control with enhanced thermometry features, as previously described.22 Powder samples for magnetic measurements were loaded in gelatin capsules. The direct current (DC) magnetization temperature dependence was obtained by cooling in zero-field and collecting the data on warming. The remanent magnetization was taken in zero applied field upon warming after cooling in a 5 Oe field. Alternating current (AC) susceptibilities were measured at 10, 100, and 1000 Hz. In addition to correcting for the diamagnetic contribution from the sample holder, the core diamagnetic corrections of −136 (1), −146 (2), and −176 × 10⁻⁶ emu/mol (3) were used.

Powder X-ray diffraction (XRPD) measurements for Rietveld structure analysis were performed at Beamline X16C of the National Synchrotron Light Source at Brookhaven National Laboratory. The powdered samples were held in a 1.0 mm diameter thin-wall quartz capillary. X-rays of wavelength 0.70025(1), 0.69731(1), and 0.70051(2) Å were selected by a Si(111) channel cut for K2Mn[Mn(CN)6], Rb₃Mn[Mn(CN)6], and Cs₃Mn[Mn(CN)6], respectively. Diffraction X-rays were selected by a Ge(111) analyzer and detected by a scintillation counter. The incident intensity was monitored by an ion chamber and used to normalize the measured signal. The TOPAS-Academic program was used to index, solve, and refine the crystal structures.23–25 Additional XRPD patterns were collected on all samples with a Bruker D8 Diffractometer (Cu Kα) using Mica (NIST Standard Reference Material 675) as an internal standard.

K₃MnII[MnII(CN)₆] Method A (1a).11 To a ~2 mL aqueous solution of MnCl2·4H2O (100 mg, 0.505 mmol) was added a ~2 mL aqueous solution of KCN (100 mg, 1.54 mmol). A gray precipitate immediately formed turning yellow then green within 5 min. After 3 h of stirring, the green powder was collected by filtration, washed with water, ethanol, acetone, and diethyl ether, and dried under vacuum at room temperature for 12 h (Yield: 70 mg, 80%). IR (KBr), v(HO, 3628 (m), v(C-CN) 2023 (sh) cm⁻¹. Caled for C₆K₂Mn₂N₆: C, 20.94; H, 0.00; N, 24.42; obs C, 20.61; H, <0.20; N, 24.30.

Method B (1b). To a ∼2 mL colorless aqueous solution of Mn(O₂CMe)₂·4H₂O (100 mg, 0.408 mmol) was added a ∼2 mL aqueous solution of KCN (80 mg, 1.22 mmol). The color change of the precipitate was the same as observed for 1a. After stirring for 3 h, the green powder was collected by filtration, washed with 2 × 10 mL water and 2 × 10 mL diethyl ether, and dried under vacuum at room temperature for 12 h (Yield: 48 mg, 69%). IR (KBr), νOH 3628 (m), νCN 2057 (s), 2023 (sh) cm⁻¹. Calcd for Cs₂K₂Mn₂N₆: C, 16.49; H, 0.00; N, 15.80; obs C, 15.14; H, < 0.20; N, 15.24.

Method C (1c). To a 5 mL colorless aqueous solution of MnCl₂·4H₂O (250 mg, 1.26 mmol) was added a 5 mL aqueous solution of KCN (329 mg, 5.05 mmol). The color change of the precipitate was the same as observed for 1a. After stirring for 3 h, the product was collected by filtration and washed with 2 × 10 mL water and 2 × 10 mL diethyl ether, and dried under vacuum at room temperature for 3 h (Yield: 211 mg, 97%). IR (KBr), νOH 3624 (s), 2057 (s), 2023 (sh) cm⁻¹. Calcd for Cs₂K₂Mn₂N₆: C, 20.94; H, 0.00; N, 24.42; obs C, 20.79; H, < 0.20; N, 23.96.

Method D (1d). To a 5 mL colorless aqueous solution of Mn(O₂CMe)₂·2H₂O (250 mg, 1.20 mmol) was added a 5 mL aqueous solution of KCN (389 mg, 5.97 mmol). The color change in the precipitate is the same as observed for 1a. After stirring for 3 h, the green solid was collected by filtration, washed with 3 × 10 mL water and 2 × 10 mL diethyl ether, and dried under vacuum at room temperature for 2 h (Yield: 160 mg, 65%). IR (KBr), νOH 3616 (s), 2059 (m) cm⁻¹. Calcd for Cs₂K₂Mn₂N₆: C, 16.49; H, 0.00; N, 15.80; obs C, 15.14; H, < 0.20; N, 18.89.

Method E (1e). A 5 mL MeOH solution of Mn(O₂CMe)₂ (250 mg, 1.44 mmol) was added to ∼15 mL MeOH solution KCN (329 mg, 5.05 mmol). The color change of the precipitate was the same as observed for 1a. After stirring for 3 h, the green solid was collected by filtration, washed with 3 × 10 mL MeOH, and dried under vacuum at room temperature for 2 h (Yield: 160 mg, 65%). IR (KBr), νOH 3624 (s), 2059 (m) cm⁻¹. Calcd for Cs₂K₂Mn₂N₆: C, 16.49; H, 0.00; N, 15.80; obs C, 15.14; H, < 0.20; N, 18.89.

**Rb₂Mn⁷⁺[Mn⁴⁺(CN)₆]₂** (2). To a 5 mL aqueous solution of Mn(OAc)₂·2H₂O (172 mg, 0.701 mmol) was added a 5 mL aqueous solution containing RbCN (352 mg, 3.16 mmol). A gray precipitate immediately formed, and turned green within 5 min, and the mixture was stirred for an additional 2 h. The green powder was collected by filtration and washed with 3 × 10 mL of water, and 3 × 10 mL of diethyl ether, and dried under vacuum over P₂O₅ for 12 h (Yield: 145 mg, 96%). IR (KBr), νOH 3628 (cm⁻¹) and νOH absorption at 3628 cm⁻¹, which is assigned as an OH bending mode. Hence, surface hydration does not appear. Use of D₂O in the preparation of 1b, or addition of D₂O to solid 1a, leads to the shifting of this absorption to 2677 cm⁻¹, as expected for deuterium substitution; thus, this peak is assigned to water. Also, the weak absorption at 1675 cm⁻¹ for 1a, taken as a Nujol mull, is assigned as an OH bending mode. Hence, surface hydration occurs for samples prepared in water.

The aqueous preparation of K₂Mn[Mn(CN)₆] from KCN and MnCl₂·4H₂O (1a), or with Mn(OAc)₂·4H₂O in a ∼3:1 ratio (1b), exhibits a sharp νOH absorption at 3628 cm⁻¹ in the IR spectra (Figure 1) that is characteristic of free (nonhydrogen bonded) water or hydroxide. The two previous studies of K₂Mn[Mn(CN)₆] did not report this peak. When the reaction was carried out with an excess of KCN in water with MnCl₂ (1e) or with Mn(OAc)₂ (1d) in a ∼5:1 ratio this absorption was minimal. In contrast, when prepared with Mn(OAc)₂ in methanol (∼3:1) (1e), this absorption does not appear. Use of D₂O in the preparation of 1b, or addition of D₂O to solid 1a, leads to the shifting of this absorption to 2677 cm⁻¹, as expected for deuterium substitution; thus, this peak is assigned to water. Also, the weak absorption at 1675 cm⁻¹ for 1a, taken as a Nujol mull, is assigned as an OH bending mode. Hence, surface hydration occurs for samples prepared in water.

1a to 1e have identical νCN IR stretching bands [and X-ray powder diffraction patterns (vide infra)]. The νCN absorption and shoulder of K₂Mn[Mn(CN)₆] (1a–e) occur at 2058 and 2023 cm⁻¹ (Figure 1) and occur at 2064 and 2028 cm⁻¹ for Rb₂Mn[Mn(CN)₆] (2). These are consistent with the νCN of [Mn⁴⁺(CN)₆]⁺ in PBA₅s (< 2100 cm⁻¹). The former value is in accord with 2055 ± 4 cm⁻¹ previously reported for K₂Mn[Mn(CN)₆]. These frequencies are lower than those predicted.
The lower traces for each plot are the differences, measured as the absorptions shifted to lower frequency by acyanometalates with only M coordinated to the cyanide of trivalent Mn III [{Mn III (CN) 6}] (2138 cm⁻¹), and K3[Mn III (CN) 6] (2183 cm⁻¹). The two peaks are attributed to the asymmetric CN stretching modes arising from a metal ion consistent with the observed low-symmetry structure. Furthermore, absorptions at 2138, 2121, or 2097 cm⁻¹ characteristic of Mn II [{Mn II (CN) 6}], K2[Mn II (CN) 6]²⁺, or [NBu₄]₃[Mn III (CN) 6]²⁻ are not observed. Evidence for the oxidative hydrolysis of Mn₃O₄ was also not observed.

Cs₂Mn IV[III] (CN) 6 (3) has been prepared for the first time and has a vCN absorption at 2073 cm⁻¹, but does not have any absorptions assignable to νOH. The bridged vCN absorption in 3 is ~15 cm⁻¹ higher in frequency than those observed for 1. This indicates that Mn–C bonding in 3 is weaker than in 1. The presence of one vCN absorption indicates O₆ symmetry, and is expected for a Prussian-blue structured material (vide infra).

**Thermal Properties.** The TGA traces for both 1a and 1b (Figure 2) show the weight loss to be <0.25% upon heating up to 150 °C, and 6 ± 2% weight loss upon heating up to 500 °C. The former value sets the upper limit of 0.05H₂O per formula. This small amount of the water implies the absence of water in the lattice. This is in accord with the observation that the intensity of the νOH peaks in 1a and 1b is attenuated upon heating to 70 °C for 14 h, but without a change in cell parameters, as evidenced from the XRPD pattern. The 6% weight loss below 500 °C indicates that K₂Mn₂(MnIV(CN) 6)₃ is relatively thermally stable lattice because of the interaction of cyanide with the K⁺. In contrast, Fe[Mn(CN) 6] loses all of its cyanides below 500 °C. Furthermore, M[Mn(CN) 6]₃(M = V, Cr, Mn, Co, Ni) decomposes below 400 °C. This suggests that the K⁺ in the K₂Mn IV[III] (CN) 6 plays an important role of its thermal stability. Compounds 1c and 1d, are similar to 1a.

**Structure.** The structures of 1 and 2 were solved by the simulated annealing method, and refined from the synchrotron powder diffraction data (Figure 3), and the structure of 3 was refined as the expected Prussian blue.

| Table 1. Summary of Crystallographic Parameters for K₂Mn IV[III] (CN) 6, 1a, Rb₂Mn IV[III] (CN) 6, 2, and Cs₂Mn IV[III] (CN) 6, 3 |
|-----------------|-----------------|-----------------|
| K₂Mn IV[III] (CN) 6, 1a | Rb₂Mn IV[III] (CN) 6, 2 | Cs₂Mn IV[III] (CN) 6, 3 |
| MW, g/mol | 344.2 | 436.92 | 531.8 |
| α, ° | 10.1786(1) | 10.4102(1) | 10.6061(1) |
| β, ° | 7.4124(1) | 7.4492(1) | 10.6061(1) |
| c, Å | 6.9758(1) | 7.2132(1) | 10.6061(1) |
| V, Å³ | 356.30(1) | 355.36(1) | 1193.06(4) |
| Z | 2 | 2 | 4 |
| space group | P2₁/n | P2₁/n | Pmnm |
| ωcalc, g/cm³ | 1.309 | 1.145 | 1.117 |
| Rp (Rwp, Rexp) | 0.060 | 0.054 | 0.079 |
| T, K | 293 | 293 | 293 |
| GOF (Rwp/Rexp) | 1.046 | 0.048 | 0.071 |

structure. At the final refinement step, all atoms were freely refined with isotropic displacement parameters (IDP). The C and N atoms of each cyano group were set to have the same IDP value. The present powder diffraction measurements do not clearly distinguish the orientation of the cyano groups; they were assigned from their bond lengths. In the Cs$_2$Mn[($\text{Mn(III)}$ (CN)$_6$)$_2$], previously reported for Na$_4$[Mn(CN)$_6$] with bond lengths of 1.98 Å for Na$_4$[Mn(CN)$_6$], their bond lengths were described as individual peaks whose centroid position, integrated intensity, and full width at half maximum were freely varied in the Rietveld process. Therefore, the structural model of Cs$_2$Mn[($\text{Mn(III)}$ (CN)$_6$)$_2$] was affected only by the sharp Bragg reflections. The crystallographic data for 1a, 2, and 3 are summarized in Table 1. The monoclinic unit cell of 1 differs from the cubic $a = 10.15$ Å previously reported for 1, hence, 1 is not a face-centered cubic that is typical of Prussian blue structured materials. 9,12

K$_2$Mn[($\text{Mn(III)}$ (CN)$_6$)$_2$] (1a) and Rb$_2$Mn[($\text{Mn(III)}$ (CN)$_6$)$_2$] (2). Both K$_2$Mn[($\text{Mn(III)}$ (CN)$_6$)$_2$] (1a) and Rb$_2$Mn[($\text{Mn(III)}$ (CN)$_6$)$_2$] (2) are isostructural. The structure of 1a is composed of six C-bound cyanides to a Mn(II) ion, and has two shorter Mn–C distances of 1.90(1) and 1.92(1) Å, and a longer distance of 2.01(1) Å. Figure 4a. This is attributed to a slight tetragonally elongated, Jahn–Teller distorted low-spin Mn$^{\text{III}}$ by ~0.1 Å. The other Mn(II) ion is high spin, and it bonds to 6 Ns with similar Mn–N bond lengths [2.18(1), 2.23(1), and 2.25(1) Å]. Figure 4b. For comparison, the Mn$^{\text{II}}$–C bond distances vary between 1.91 and 1.98 Å for Na$_4$[Mn(CN)$_6$]·10H$_2$O. 31a,b The Mn–C distances are 1.90(2), and 1.92(2) Å and slightly tetragonally elongated 1.97(2) Å, and the Mn–N distances are 2.22(1), 2.23(1), and 2.24(1) Å for 2. The Mn$^{\text{III}}$–N bond for Na$_4$[($\text{Mn(II)}$ (CN)$_6$)$_2$] is 2.207(9) Å, 13 and that for Mn$_3$[Co(CN)$_6$]$_2$·12H$_2$O is 2.184(9) Å. 31c Hence, this is a non-distorted high-spin Mn$^{\text{III}}$ ion. The CN bond distance (~1.14 Å) is not sensitive to the chemical environment. 10,31a,e

The Mn–C–N angles of 168.7(9), 172.9(7), and 178(1)$^\circ$ (average = 173$^\circ$) for 1a, and 176(2), 177(1), and 179(1)$^\circ$ (average 177$^\circ$) for 2 approach linearity, as expected. However, the Mn–N–C angles of 152.7(7), 148.2(7), and 145.6(7)$^\circ$ (average = 148.8$^\circ$) for 1, and 150(1), 153(1), and 157(1)$^\circ$ (average = 153.3$^\circ$) for 2 deviate substantially from linearity, an unexpected result for a Prussian blue structured material.

Each cyano bridge a low- and a high-spin Mn(II) ion to form a three-dimensional (3-D) framework structure with void spaces occupied by K$^+$ (1a, Figures 4 and 5) or Rb$^+$ ions (2). The Mn$^{\text{II}}$–Mn$^{\text{II}}$ separations are 5.09 and 5.19 Å for 1a and 2, respectively, which are slightly shorter than the Mn–Cr separations in Na$_4$[($\text{Mn(II)}$ (CN)$_6$)$_2$] (5.41 Å) [and 5.30 Å for Cs$_2$Mn[($\text{Mn(III)}$ (CN)$_6$)$_2$] (vide infra)] that also possesses nonlinear Mn–N–C bonding. As a consequence, MnC$_6$, and MnN$_6$ occur in alternating rows and have their octahedra tilting in opposing directions (Figure 5). The K$^+$ and Rb$^+$ ions interact with seven cyanide nitrogens with K$^+$–N and Rb$^+$–N distances that range from 2.98 to 3.50 Å, and 3.15 and 3.59 Å for 1 and 2, respectively. The alkali ion interactions with the cyanide ligands occurs in all directions, and leads to a 3-D zigzag network of the Mn–CN–Mn bonds. Due to the observation of the v$_{OH}$ absorption for 1a, crystallographic evidence was sought, but could not be identified, in the Fourier difference map, and is in accord with the presence of surface water.

In contrast to a cubic Prussian blue structural motif where the void spaces are defined by the cubic framework arrangement of atoms arising from covalent Mn–CN and Mn–NC bonding leading to linear Mn–CN–M’ angles, the less covalent Mn$^{\text{III}}$ (more ionic) can accommodate a reduced Mn–CN–M’ angle induced from the electrostatic interactions increase with decreasing cation size (K$^+$ > Rb$^+$ > Cs$^+$) minimizing void space, as occurs. Similar, bent cyanide bridged ligands with nonlinear Mn–N–C angles of 152.7 and 153.4$^\circ$ have been observed for A[($\text{Me}_{3}\text{tacn}$)$_3$Mn$_3$(CN)$_6$]Br$_2$ClO$_4$ (A = Na, K; Me$_3$tacn = N,N,N’-trimethyl-1,4,7-triazacyclonane).


also possessing high spin Mn$^{II}$. Likewise, Zn–N–C
angles ranging from 151.4 and 165.1° have been reported
for Zn$_3$[M$^{III}$(CN)$_6$]$_2$ ($M =$ Fe, Co), Zn$_3$A$_2$[Fe$^{III}$(CN)$_6$]$_2$
($A =$ Rb$^+$, NH$_4^+$) possessing ionic Zn$^{II}$,33b and an even
further reduced Cu$^{II}$–N–C angle of 120.1° has been
documented.33c

Cs$_2$Mn$^{II}$[Mn$^{II}$(CN)$_6$]$_3$ (3). Cs$_2$Mn$^{II}$[Mn$^{II}$(CN)$_6$]$_3$ (3) ex-
hibits the typical cubic Prussian Blue structure34 [a =
10.6061(1) Å] with one hexacoordinate Mn(II) sur-
rrounded by six 6 C-bound cyanides, with linear
MnCNMn linkages. The Mn–C, Mn–N, and C–N
distances are 1.93(1), 2.19(1), and 1.18(1) Å, respectively,
Figure 6. Hence, structural evidence for Jahn–Teller
distortion about the low spin Mn(II) site is not present.
The Mn(II)···Mn(II) separation is a/2 (5.303 Å). The
cubic unit cell is very similar to that of NaMn[Cr(CN)$_6$]
[a = 10.8159(12) Å].12 Hence, 3 has a structure that is
typical of Prussian blue.

Comparison of the A$_2$Mn$^{II}$[Mn$^{II}$(CN)$_6$]$_3$ (A = K, Rb, Cs)
Structures. The A$_2$Mn$^{II}$[Mn$^{II}$(CN)$_6$]$_3$ (A = K, Rb) struc-
tural motif is unusual and differs from the well-known fcc
Prussian blue motif33c as a consequence of its monoclinic
unit cell. Perspective views of the Prussian blue and
Rb$_2$Mn$^{II}$[Mn$^{II}$(CN)$_6$]$_3$ structures are shown in Figure 7.
The new motif is related to the Prussian blue lattice
parameters that are approximately a, a/√2, a/√2, β ∼
90°. The distortion from an orthorhombic lattice is small,
but it is clearly required by the raw data, as shown by
profile fits in the Supporting Information, Figures S3 and
S4. The nonlinear Mn–C–N–Mn linkages for the latter
lead to canting of the octahedra, as described above
(Figure 5), and buckling of the 3-D lattice, Figure 7. This
is also observed looking down the a-axis, Figure 8. For
both structure types 3-D channels are present that are
filled by the alkali cations, Figure 8.

The observed XRPD pattern of 3 can also be equally well-explained
with the Fm3c space group symmetry whereby all C and N are positionally
disordered, but this was discarded, as it is inconsistent with the structure of
the other PBAs, and the magnetic data.

Magnetic Properties. The magnetic susceptibilities, χ(T),
of 1–3 as well as K$_4$[Mn(CN)$_6$]·3H$_2$O were measured
between 5 to 300 K, and are plotted as χT(T), Figures 9
and 10, and the results are summarized in Table 2. [See
Supporting Information, Figures S1 and S2 for the χ(T)
data.] K$_4$[Mn(CN)$_6$]$_3$ has a room temperature χT value of
0.50 emu K/mol that exceeds the low-spin spin-only value
0.375 emu K/mol for Mn$^{II}$ indicative of an orbital contribution
and g = 2.31. The χT value decreases slightly with decreasing
temperature to 0.45 emu K/mol at 60 K, followed by a big
decrease to 0.275 emu K/mol at 2 K, indicating either an intermolecular interaction or a spin–orbit interaction (λ). For K$_4$[Mn(CN)$_6$]$_3$, it is known
that the magnetic moment has a range of 0.48 to 0.59 emu
K/mol,17 and attempts to obtain the spin–orbit interaction
(λ) for K$_4$[Mn(CN)$_6$]$_3$ were unsuccessful because of the large
deviation below ∼100 K.

K$_2$Mn$^{II}$[Mn$^{II}$(CN)$_6$]$_3$ (1). 1a and 1e have room-temperature
χT values of 5.56 and 5.10 emu K/mol, respectively, and
like the previously reported values of 4.999 and 5.133 emu
K/mol for K$_2$Mn[Cr(CN)$_6$] exceed the 4.75 emu K/mol
expected for the spin-only value for one low- and one high-
spin Mn(II) site. This is indicative of an anisotropic orbital
contribution from the low spin Mn(II), and the differing
average orientations of the polycrystalline samples. These
values decrease upon cooling and reach shallow minima of
4.99 and 5.11 emu K/mol at 90 and 105 K, respectively,
and then increase and reach maxima of 100 ± 2 emu K/mol
at 32 ± 1 K for 1a and 1e, Figure 10. Above 120 K, the χ$^{-1}$(T)
can be fit to the Curie–Weiss expression, χ ∝ \( (T - \theta)^{-1} \),
with \( \theta = -63 \pm 3 \) K, indicating significant antiferromag-
netic couplings. The significant increase in χT(T) at low
temperature suggests the onset of magnetic ordering. Like-
wise, previously K$_2$Mn[Cr(CN)$_6$] was reported to reach a
minimum at 105 K, and then increase and reach maxima of
1325 emu K/mol at 24 K as well as \( \theta = -19 \) K from data
taken between 100 and 290 K.35

A fit of the χ$^{-1}$(T) data to the Néel hyperbolic equation,
eq 1 \( \times \) where \( C \) and \( \theta \) are the Curie and Weiss constants,
respectively, and \( \theta' \) and \( \xi \) are proportional to \( \eta_A \eta_B C (\eta_A - \eta_B) \) and \( \eta_A \eta_B C \) (where \( \eta \) is the fractional occupancy of
each sublattice site), respectively.\(^{35}\) (Figure 11) gives a \(T_c\) of 41 K for both 1a and 1e.

\[
\chi^{-1} = \frac{T - \theta}{C} - \frac{\zeta}{T - \theta'} \tag{1}
\]

The field-cooled (FC) and zero-field-cooled (ZFC) magnetizations for 1a and 1e were measured in a 5 Oe magnetic field (Figure 12). The bifurcation temperature, \(T_b\), of the FC/ZFC magnetizations of 47 and 46 K for 1a and 1e, respectively.

The 5 K field dependence of the magnetization, \(M(H)\), shows a rapid rise with increasing field, \(H\), with respect to...
the expectation from the Brillouin expression, is suggestive of magnetic ordering for \(1a\) and \(1e\) (Figure 13). The 50 kOe magnetizations at 5 K are 16, 100, and 15,800 emu Oe/mol for \(1a\) and \(1e\), respectively, but are still gradually rising with increasing field. Hence, they are in accord with the expectation of 22,340 emu Oe/mol for antiferromagnetic coupling leading to ferrimagnetic ordering, and are consistent with the reported 70 kOe magnetization at 4.5 K that is 24,000 emu Oe/mol for K\(_2\)Mn[Mn(CN)\(_6\)]\(_8\). 8 At 5 K the remanent magnetizations, \(M_r\), are 8600 and 9350 emu Oe/mol, and the coercive fields, \(H_{cr}\), are 3900 and 9150 Oe for \(1a\) and \(1e\), respectively (Figure 13). Hence, the biggest difference between the sample that has a \(\nu_{OH}\) absorption (i.e., \(1a\)), and the one that does not (i.e., \(1e\)), is the more than doubling of the \(H_{cr}\), but in both cases they exceed the previously reported value of 370 Oe. 8

In addition, peaks in both the frequency-independent in-phase, \(\chi'(T)\), and out-of-phase, \(\chi''(T)\), components of the AC susceptibility for \(1a\) and \(1e\) occur, and are characteristic of ferri- or ferromagnetic ordering, Figure 14. Using the maximum in the 10 Hz \(\chi'(T)\) data, \(T_c = 38\) K, which is a bit reduced from the bifurcation temperature, \(T_b\).

The 41 K \(T_c\) for K\(_2\)Mn[Mn(CN)\(_6\)]\(_8\) is in contrast to that of the isoelectronic Fe\(_{III}\)[Fe\(_{III}\)(CN)\(_6\)]\(_4\)H\(_2\)O with low spin Fe\(_{III}\) (t\(_{2g}\)^5, \(S = 1/2\)) and high spin Fe\(_{III}\) (t\(_{2g}\)^2e\(_g^2\), \(S = 5/2\))

\[a\] 4.5 K, 70 kOe. \[b\] Not reported. \[c\] Not saturated. \[d\] 19,150 emu Oe/mol at 90 kOe.
that exhibits a lower $T_c$ of 17.4 K and $H_{cr}$ of 465 Oe.\textsuperscript{36} Fe$^{III}$[Fe$^{III}$](CN)$_6$·4H$_2$O possesses a fcc structure with water molecules in the interstitial sites. Thus, the bent Mn-CN-Mn bond contributes to the higher magnetic ordering temperature and coercive field of K$_2$Mn[Mn(CN)$_6$] compared to Fe$^{III}$[Fe$^{III}$](CN)$_6$·4H$_2$O. The Mn$^{II}$·Mn$^{III}$ separations of 5.09 Å are identical to the Fe$^{III}$·Fe$^{III}$ distance of 5.1090(5) Å; thus, the bent cyanide bridges, rather than the short distance between the spin centers, play a crucial role in the superexchange mechanism. The more ionic character (less directional covalency) associated with Mn$^{II}$ with respect to Fe$^{II}$\textsuperscript{32} accommodates the significantly reduced Mn–N–C angle with respect to the Fe–N–C angle, stabilizing the observed solvent-free non-Prussian blue structure.

Rb$_2$Mn$^{III}$[Mn$^{II}$](CN)$_6$ (2). The room temperature $\chi T$ value for 2 is 4.83 ± 0.07 emu K/mol, and is also in accord with 4.75 emu K/mol expected for the spin-only value for one low- and one high-spin Mn$^{II}$ site (Figure 8).\textsuperscript{37} The $\chi T(T)$ decreases upon cooling and reaches a minimum of 4.40 emu K/mol at 100 K, before again increasing to 117 emu K/mol at 28 K. Above 170 K, the $\chi^{-1}(T)$ data can be fit to the Curie–Weiss expression with $\theta = -30$ K, indicating antiferromagnetic coupling, albeit weaker, than observed for 1a and 1e. The large increase in $\chi(T)$ at low temperature suggests the onset of magnetic ordering. The $T_c$ of 34.6 K was obtained from fitting the data to Néel's hyperbolic equation, eq 1 (Figure 11).\textsuperscript{8,10} This is reduced from 41 K for K$_2$Mn-[Mn(CN)$_6$].

The 1 Oe FC/ZFC magnetizations for 2 exhibit a $T_c$ of 38 K (Figure 15, $H \leq 10$ Oe). Unlike for 1a and 1e, the ZFC magnetizations exhibit an anomaly (bump) at ~34 K, whose intensity increases with applied field (Figure 15). This suggests a transition to a second magnetic phase upon cooling; however, the nature of this is unknown, but might arise from canting. To rule out an extrinsic impurity, an independent sample was studied, and the magnetic data were in quantitative agreement.

The 5 K $M(H)$ shows a rapid rise with increasing field, $H$, which with respect to the expectation from the Brillouin expression is suggestive of magnetic ordering (Figure 13). At 90 kOe the magnetization is 19,250 emu Oe/mol and still rising; hence, it is in accord with the expectation of 22,340 emu Oe/mol for antiferromagnetic coupling leading to ferrimagnetic ordering. As shown in Figure 13, 2 has a significant coercive field of 8850 Oe, remanent magnetization, $M_r$, of 9300 emu Oe/mol at 5 K, and the hysteresis is almost identical to that for 1e (Figure 13).

In addition, peaks in both the frequency-independent $\chi'(T)$ and $\chi''(T)$ for 2 occur and are characteristic of ferri- or ferrimagnetic ordering. Figure 16. Using the maximum in the 10 Hz $\chi(T)$ data, $T_c = 34$ K, which is a bit reduced from the 38 K bifurcation temperature, $T_b$, $\chi'(T)$ has a shoulder at ~29 K and $\chi''(T)$ exhibits a second

\textsuperscript{37} It is also substantially greater than the 1.0 emu Oe/mol expected for two low-spin, $S = 1/2$ Mn$^{II}$ ($g \sim 2.3$) sites, and is substantially lower than the 8.75 emu Oe/mol expected for two high-spin, $S = 5/2$ Mn$^{II}$ ($g \sim 2.0$) sites.

absorption at $\sim 30$ K that are suggestive of an unknown second magnetic phase, and is also indicated from the FC/ZFC magnetization data, Figure 15.

$\text{Cs}_2\text{Mn}^{II}[\text{Mn}^{II}(\text{CN})_6]_3$. The room temperature $\chi T$ value for 3 is 4.68 emu K/mol, and like 1a to 1e, is in accord with 4.75 emu K/mol expected for the spin-only value for one low- and one high-spin Mn(II) site (Figure 9). 38 $\chi T(T)$ decreases upon cooling and reaches a minimum of 3.46 emu K/mol at 26 K, before again increasing to 6.3 emu K/mol at 22 K. Above 25 K, the $\chi^{-1}(T)$ data can be fit to the Curie–Weiss expression with $\Theta = -15$ K, indicating antiferromagnetic coupling, albeit weaker, than observed for 1a, 1e, 2, and 3. The increase in $\chi T(T)$ at low temperature suggests the onset of magnetic ordering.

The 5 Oe FC/ZFC magnetizations for 3 (Figure 17) exhibit a $T_b$ of 24 K. The $T_c$ of 21 K was obtained from fitting the data to Néel’s hyperbolic equation, eq 1, (Figure 11). 38 This is reduced from that reported for 1a and 1e.

The magnetization at 50 kOe is 9360 emu Oe/mol and is still rising without evidence of saturating. As shown in Figure 18, 3 has a significant coercive field of 5000 Oe and remanent magnetization of 640 emu Oe/mol at 5 K, and the shape of the hysteresis curve is quite unusual. The source of the unusual shape of the $M(H)$ curve, the high coercivity, and lack of approaching saturation is unknown.

Peaks in both $\chi'(T)$ and $\chi''(T)$ characteristic of ferri- or ferromagnetic ordering are also observed, Figure 19. Using the maximum in the 10 Hz $\chi'(T)$ data, a $T_c$ of 22 K, that is reduced from the bifurcation temperature, $T_b$, is observed. The $\chi'(T)$ data of 3 has a small frequency dependence with the temperatures of each maximum being almost constant $\{\phi \sim 0; \phi = \Delta T/T_c \Delta \log f \}$; where $T_c$ is the temperature of the peak in the lowest frequency (10 Hz) data; and $f$ is the frequency in hertz] indicating no spin glass behavior. The out-of-phase, imaginary, $\chi''(T)$ data displays a peak below 24 K, indicating magnetic ordering.

**Conclusion**

$K_2\text{Mn}[\text{Mn}(\text{CN})_6]$ was made in aqueous (1a) or non-aqueous (1e) media. 1a has a sharp $\nu_{\text{OH}}$ absorption in the IR
spectrum, while \( \text{Ie} \) does not. Use of \( \text{D_2O} \) shifts this peak as expected for deuteration. While this supports the presence of \( \text{H}_2\text{O} \), that is not evident from the structure, TGA, XRPD, or elemental analysis; thus, it is attributed to surface water, and it may arise from surface hydrolysis. \( \text{K}_2\text{Mn}[\text{Mn(CN)}_6] \) has a bent (148.8°) \( \text{Mn}^-\text{CN}^-\text{Mn}^- \) framework that is different with respect to the face-centered structures typical of PBAs. This nonlinearity is attributed to the ionic nature if high spin Mn(II) strong interactions between \( \text{K}^+ \) and cyanide ions. \( \text{Ia} \) and \( \text{Ie} \) exhibit essentially identical structures and similar magnetic properties. \( \text{Rb}_2\text{Mn}[\text{Mn(CN)}_6] \) (2) is isostructural to \( \text{K}_2\text{Mn}[\text{Mn(CN)}_6] \); however, the longer \( \text{Rb}^+ \cdot \cdot \cdot \text{N} \) distances with respect to \( \text{K}^+ \cdot \cdot \cdot \text{N} \) provide weaker electrostatic interactions decreasing the nonlinearity of the \( \text{Mn}^-\text{N}^-\text{C} \) linkages to 153.3°. This distortion from the traditional fcc Prussian blue structure is not observed for the isoelectronic \( \text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6] \cdot 4\text{H}_2\text{O} \) because of the greater charges and greater covalency (reduced ionic character).

\( \text{Cs}_2\text{Mn}[\text{Mn(CN)}_6] \) has the archetypal fcc Prussian blue structure and is magnetically characterized to order as a ferrimagnet at 21 K. While saturation does not occur at 50,000 Oe, it has a remanent magnetization of 640 emu Oe/mol and a large coercive field of 5 kOe at 5 K. The latter is attributed to the positional disorder of the cyanides.

The 41 K \( T_c \) for \( \text{K}_2\text{Mn}[\text{Mn(CN)}_6] \) is in contrast to isoelectronic \( \text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6] \cdot 4\text{H}_2\text{O} \) with low spin \( \text{Fe}^{\text{III}}(t_{2g}^5 \cdot S = 1/2) \) and high spin \( \text{Fe}^{\text{III}}(t_{2g}^2 \cdot e_g^2 \cdot S = 5/2) \) that exhibits a lower \( T_c \) of 17.4 K and \( H_{\text{cr}} \) of 465 Oe.\(^{16}\) The \( T_c \) is comparable to that for Prussian blue structured 3. Furthermore, \( T_c \) increases as \( \text{K}^+ > \text{Rb}^+ > \text{Cs}^+ \) for \( \text{A}_2\text{Mn}[\text{Mn(CN)}_6] \) (\( \text{A} = \text{K}, \text{Rb}, \text{Cs} \) and this correlates with the increasing deviation of linearity of the \( \text{Mn}^-\text{N}^-\text{C} \) linkages of 31.2 (K) > 26.7 (Rb) > 0° (Cs\(^+ \)), Figure 20, and decreasing \( \text{Mn}^{\text{II}^-} \cdot \cdot \cdot \text{Mn}^{\text{II}^-} \) separations of 5.09 (K) < 5.19 (Rb) < 5.30 Å (Cs\(^+ \)). This suggests that the bent cyanide bridges play a crucial role in the superexchange mechanism by increasing the coupling via shorter \( \text{Mn}^{\text{II}^-} \cdot \cdot \cdot \text{Mn}^{\text{II}^-} \) separations, and perhaps enhanced overlap. MO calculations are needed to provide insight into this. Furthermore, use of the smaller Na\(^+ \) cation should lead to stronger interactions increasing \( T_c \), and increasing pressure should lead to greater deviation of the \( \text{MnNC} \) angle from linearity and increase \( T_c \).

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**Supporting Information Available:** The powder X-ray crystallographic information files (CIF) for \( \text{K}_2\text{Mn}[\text{Mn}^{\text{III}}(\text{CN})_6] \), \( \text{Rb}_2\text{Mn}[\text{Mn}^{\text{III}}(\text{CN})_6] \), and \( \text{Cs}_2\text{Mn}[\text{Mn}^{\text{III}}(\text{CN})_6] \) (CCDC 709700, 723397, and 709701), \( \chi(T) \) for \( \text{K}_4[\text{Mn(CN)}_6] \), \( \text{Ia}, \text{Ie}, 2 \), and 3, and fits of the observed PXRD data for \( \text{Ia} \) and 2 assuming orthorhombic and monoclinic space groups. This material is available free of charge via the Internet at http://pubs.acs.org.