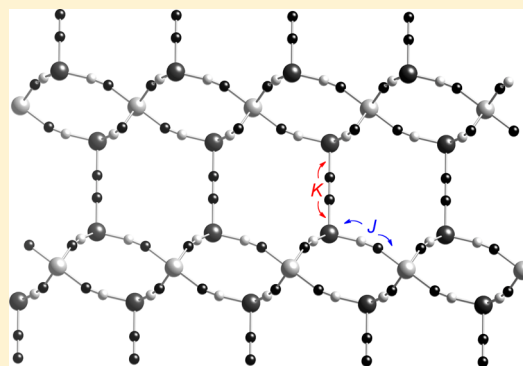


# A Mean-Field Analysis of the Exchange Coupling ( $J$ ) for Noncubic Prussian Blue Analogue Magnets

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## Supporting Information

**ABSTRACT:** Mean field expressions based on the simple Heisenberg model were derived to correlate the intra- and interlayer exchange couplings to the critical temperatures,  $T_c$ , for three metalocyanide-based magnets with extended 2- and 3-D structure types. These expressions were used to estimate the exchange coupling,  $J$ , for 2-D ferrimagnetic  $[\text{NEt}_4]_2\text{Mn}^{\text{II}}_3(\text{CN})_8$ , 3-D antiferromagnetic  $[\text{NEt}_4]\text{Mn}^{\text{II}}_3(\text{CN})_7$ , and 3-D antiferromagnetic interpenetrating 3-D  $\text{Mn}^{\text{II}}(\text{CN})_2$ . The type and magnitude of the exchange coupling are in accord with the previously reported magnetic data.

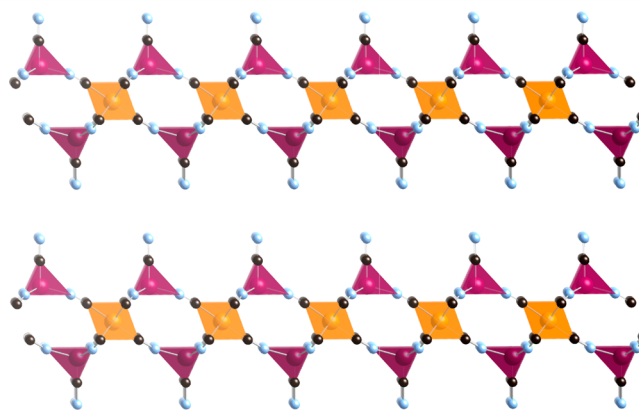


## INTRODUCTION

Many Prussian blue structured hexacyanometalates have been reported,<sup>1–4</sup> with members of this structure type having several compositions, for example,  $\text{M}'^{\text{III}}_4[\text{M}^{\text{II}}(\text{CN})_6]_3$ ,  $\text{C}^+\text{M}^{\text{III}}[\text{M}^{\text{III}}(\text{CN})_6]_2$ ,  $\text{M}^{\text{II}}_3[\text{M}^{\text{III}}(\text{CN})_6]_2$ ,  $\text{A}^+\text{M}'^{\text{III}}[\text{M}^{\text{II}}(\text{CN})_6]$ ,  $\text{A}^+_2\text{M}^{\text{II}}[\text{M}^{\text{II}}(\text{CN})_6]$ , and  $\text{M}'^{\text{III}}[\text{M}^{\text{III}}(\text{CN})_6]$  ( $\text{A}^+$  = alkali cation) that are frequently solvated. They all share the common features of (i) being face centered cubic (fcc) ( $a \approx 10.5$  Å), (ii) having the C-bonded M being low-spin and surrounded by high-spin  $\text{M}'$  that is bonded to six cyanide nitrogens, and (iii) having linear  $-\text{M}'-\text{N}\equiv\text{C}-\text{M}-\text{C}\equiv\text{N}-\text{M}'-$  linkages along the three unit cell axes, except where defect sites occur.

Recently several noncubic PBAs of  $\text{A}_2\text{Mn}^{\text{II}}[\text{Mn}^{\text{II}}(\text{CN})_6]$  ( $\text{A} = \text{Na}, \text{K}, \text{Rb}$ ) composition have been reported.<sup>5,6</sup> More interesting, when  $\text{A} = \text{NEt}_4^+$  a layered (2-D) ferrimagnet of  $[\text{NEt}_4]_2\text{Mn}^{\text{II}}_3(\text{CN})_8$ <sup>7,8</sup> (Figure 1), and 3-D bridged-layered antiferromagnet of  $[\text{NEt}_4]\text{Mn}^{\text{II}}_3(\text{CN})_7$  (Figure 2) are formed.<sup>8</sup> Furthermore, thermolysis of either  $[\text{NEt}_4]_2\text{Mn}^{\text{II}}_3(\text{CN})_8$  or  $[\text{NEt}_4]\text{Mn}^{\text{II}}_3(\text{CN})_7$  forms  $\text{Mn}^{\text{II}}(\text{CN})_2$ ,<sup>9</sup> which possesses an interpenetrating extended 3-D sphalerite (diamondoid) structure (Figure 3).  $[\text{NEt}_4]_2\text{Mn}^{\text{II}}_3(\text{CN})_8$  is a ferrimagnet while  $[\text{NEt}_4]\text{Mn}^{\text{II}}_3(\text{CN})_7$  and  $\text{Mn}^{\text{II}}(\text{CN})_2$  are antiferromagnets. All have  $\text{M}-\text{C}\equiv\text{N}-\text{M}'$  ( $\text{M} = \text{M}' = \text{Mn}^{\text{II}}$ ) linkages; however, the  $\text{MnCNMn}$  separation is longer by  $\sim 0.2$  Å when both  $\text{Mn}^{\text{II}}$  sites are tetrahedral and high spin (HS), with respect to when the  $\text{Mn}^{\text{II}}-\text{C}$  site is octahedral and low spin (LS) (Table 1), as high-spin M sites have larger radii with respect to low-spin M sites due to the presence of antibonding electrons.<sup>10</sup>

The key to understanding PBA-based magnets is the determination of the nearest neighbor exchange coupling,  $J$ , for these magnetic materials. The mean field (MF) analysis based on the Heisenberg model [ $H = -\sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$  ( $i > j$ )]<sup>11</sup> has

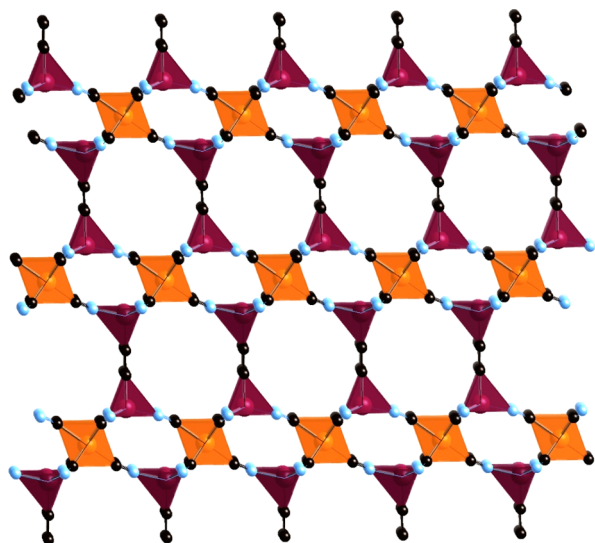


**Figure 1.** Extended 2-D network bonding observed for  $[\text{NEt}_4]_2\text{Mn}^{\text{II}}_3(\text{CN})_8$  (1) (high-spin Mn is maroon, low-spin Mn is orange, C is black, and N is blue).<sup>7</sup> The disordered anions and solvent reside between the layers.

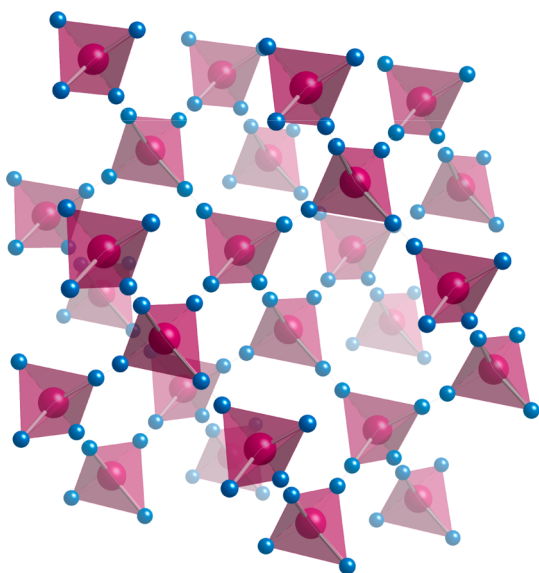
been applied to cubic PBAs,<sup>1</sup> and eq 1 has been used extensively to relate  $T_c$  with an average  $J$ . This expression is applicable for materials with one type of spin site of total spin,  $S$ , where  $z$  is the number of nearest neighbors, and  $k_B$  is Boltzmann's constant. Antiferromagnetic PBAs have yet to be reported, as PBAs have differing  $\text{M}$ ,  $\text{M}'$ ,  $S_M$ , and/or  $S_{M'}$  yielding either ferrimagnets or less commonly ferromagnets.<sup>1</sup> Hence, a MF expression for a system possessing two different adjacent spin sites,  $i$  and  $j$ , was developed, eq 2,<sup>1b,12</sup> where  $z_i$  and  $z_j$  are the number of nearest neighbors, and  $S_i$  and  $S_j$  are the total spin

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**Figure 2.** Extended bridged layer 3-D network bonding observed for  $[\text{NEt}_4]\text{Mn}^{\text{II}}_3(\text{CN})_7$  (2) (high-spin Mn is maroon, low-spin Mn is orange, C is black, and N is blue).<sup>8</sup> The disordered anions and solvent reside between the layers.



**Figure 3.** Single extended network bonding for 3-D  $\text{Mn}^{\text{II}}(\text{CN})_2$  (3) (high-spin Mn = maroon; the disordered C and N are blue).<sup>9</sup> The second, interpenetrating lattice is not shown.

on spin sites  $i$  and  $j$ , respectively, and the Landè  $g$  values for each spin site are the same. Note that the MF expressions for  $T_c$  with a single exchange interaction are the same for ferromagnetic ( $J > 0$ ) or antiferromagnetic ( $J < 0$ ) interactions.

$$T_c = \frac{|J|zS(S+1)}{3k_B} \quad (1)$$

$$T_c = \frac{|J|\sqrt{z_i z_j S_i(S_i+1)S_j(S_j+1)}}{3k_B} \quad (2)$$

As MF theory ignores the effect of topology (i.e., dimensionality) on  $T_c$ , it provides the same result for any material with the same spin ( $S$ ), exchange ( $J$ ), and bonding, regardless of structural dimensionality. Furthermore, MF theory also gives the same result for either Heisenberg or Ising spins. In the absence of anisotropy, however, long-range spin fluctuations destroy the magnetic order of a 1- or 2-D system (Mermin-Wagner theorem).<sup>11</sup> Via evaluation of the spin excitation spectrum for a 2-D system with exchange,  $J$ , the  $T_c$  rises very rapidly with anisotropy  $D$  as  $T_c \propto J/\log(J/D)$ .<sup>13</sup> Thus, MF theory provides an adequate approximation for an anisotropic 2-D material when  $D/J \gg 1$ . For  $D \approx J$ , the  $T_c$  of a 2-D material will be suppressed by long-range fluctuations, and higher  $T_c$  values will occur when the effect of those fluctuations is diminished by 3-D magnetic order. Nonetheless, for a 3-D system, MF theory may still overestimate the transition temperature by as much as 40%. Hence, MF theory is best used to estimate the ratios of exchange constants either for different materials or within the same material.

Equation 2 should work well for cubic and distorted cubic<sup>5</sup> PBAs with  $\text{M}:\text{M}'::1:1$  and the free-electron isotropic Landè  $g$  value for each spin site,<sup>1,2</sup> as none have a single spin site that is needed for eq 1. The aforementioned noncubic PBAs 1 and 2, however, are inappropriate for eq 2, and a MF analysis was performed for these structures to develop appropriate expressions, which are reported herein. Note that  $\text{Mn}(\text{CN})_2$  (3) does have a single spin site for which eq 1 is appropriate.

Although  $[\text{NEt}_4]_2\text{Mn}^{\text{II}}_3(\text{CN})_8$  (2) is a 2-D ferrimagnet with very weak interlayer interactions, the anisotropy on the low-spin  $\text{Mn}^{\text{II}}$  ions with  $S' = 1/2$  produces long-range magnetic order and justifies the application of MF theory for this compound.

The  $T_c$  values for the ferrimagnet  $[\text{NEt}_4]_2\text{Mn}^{\text{II}}_3(\text{CN})_8$  and the antiferromagnet  $[\text{NEt}_4]\text{Mn}^{\text{II}}_3(\text{CN})_7$  and  $\text{Mn}^{\text{II}}(\text{CN})_2$  were determined in several ways with some variation between methods.<sup>8,9,14</sup> To be self-consistent with our MF analysis, the same method, namely, the temperature at which the maximum in the frequency independent  $\chi'(T)$  occurs, will be used as  $T_c$ . These values are 25.7, 28.5, and 78 K for  $[\text{NEt}_4]_2\text{Mn}^{\text{II}}_3(\text{CN})_8$ ,  $[\text{NEt}_4]\text{Mn}^{\text{II}}_3(\text{CN})_7$ , and  $\text{Mn}^{\text{II}}(\text{CN})_2$ , respectively (Table 1).

Although MF theory can overestimate  $T_c$  by as much as 40%, it predicts trends and estimates of exchange constants,<sup>12</sup> and it provides better estimates for the ratios of exchange couplings in different materials. Herein, MF theory estimates the ratios of the interlayer and intralayer couplings.

**Table 1.** Summary of Structurally Characterized 2- and 3-D Noncubic PBAs and Their  $T_c$  Values

magnet	interlayer separation, Å	Mn–CN–Mn, Å	bonding dimensionality	$T_c^d$ K	type <sup>e</sup>	ref
$[\text{NEt}_4]_2\text{Mn}^{\text{II}}_3(\text{CN})_8$	1	8.074	2-D	25.7	FI	7, 8
$[\text{NEt}_4]\text{Mn}^{\text{II}}_3(\text{CN})_7$	2	14.543	3-D	28.5	AF	8
$\text{Mn}^{\text{II}}(\text{CN})_2$	3	5.325 <sup>b,c</sup>	3-D	78	AF	9

<sup>a</sup>Low spin  $\text{Mn}^{\text{II}}\text{–CN–high-spin Mn}^{\text{II}}$ . <sup>b</sup>High spin  $\text{Mn}^{\text{II}}\text{–CN–high-spin Mn}^{\text{II}}$ . <sup>c</sup>Intra- and interlattice  $\text{Mn}\cdots\text{Mn}$  separation. <sup>d</sup>From the peak in  $\chi'(T)$ . <sup>e</sup>FI = ferrimagnet; AF = antiferromagnet.

**Table 2.** Summary of the MF Expressions [ $H = -\sum J_{ij}S_i \cdot S_j$  ( $i > j$ )] for General S for 2-D and 3-D Compounds 1, 2, and 3, and Computed Inter- and Intralayer Couplings (Vide Infra)

composition (compound)	mean field (MF) expression for $T_c^a$	interlayer coupling, $K/k_B$ , K	intralayer coupling, $J/k_B$ , K
	2-D		
$[\text{NEt}_4]_2\text{Mn}^{\text{II}}_3(\text{CN})_8$ (1)	$T_c = \frac{ J }{k_B} \sqrt{2S(S+1)S'(S'+1)}$	$0^a$	$-7.1$
	3-D		
$[\text{NEt}_4]\text{Mn}^{\text{II}}_3(\text{CN})_7$ (2)	$T_c = \frac{KS(S+1) + \sqrt{K^2[S(S+1)]^2 + 72J^2S(S+1)S'(S'+1)}}{6k_B}$	$-1.8, -6.7^a$	$-7.1^b, -4.4$
$\text{M}(\text{CN})_2$ (3)	$T_c = \frac{ J zS(S+1)}{3k_B}$	$0^a$	$-6.7$

<sup>a</sup> $J$  = intralayer coupling;  $K$  = interlayer coupling. <sup>b</sup>Assumed.

## MEAN FIELD EXPRESSIONS

The MF expressions for  $T_c$ , using  $H = -\sum J_{ij}S_i \cdot S_j$  ( $i > j$ ), are determined for the noncubic layered (2-D) structure associated with  $[\text{NEt}_4]_2\text{Mn}^{\text{II}}_3(\text{CN})_8$  (1), and the 3-D bridged layer structure associated with  $[\text{NEt}_4]\text{Mn}^{\text{II}}_3(\text{CN})_7$  (2). The former 2-D layered system has two spin sites in a 1:2 ratio, and a single intralayer coupling  $J$ , while the latter 3-D system also has two spin sites in a 1:2 ratio, a single intralayer coupling,  $J$ , and single interlayer coupling,  $K$ . This paper adopts the sign convention that  $J$  or  $K > 0$  corresponds to ferromagnetic coupling.

**Compound 1.** The MF solution for the general spin case of 2-D compound 1 of  $[\text{NEt}_4]_2\text{Mn}^{\text{II}}_3(\text{CN})_8$  composition, Figure 1, was constructed (see the Supporting Material). MF theory predicts

$$T_c = \frac{|J|}{k_B} \sqrt{2S(S+1)S'(S'+1)} \quad (3)$$

where  $J$  is the coupling between the low-spin  $\text{Mn}^{\text{II}}$  ( $z = 6$ ) with spin  $S$ , and the high-spin  $\text{Mn}^{\text{II}}$  ( $z = 3$ ) within the layers with  $S'$ .

**Compound 2.** The MF expression for the general spin case for 3-D 2 of  $[\text{NEt}_4]\text{Mn}^{\text{II}}_3(\text{CN})_7$  composition, Figure 2, was constructed (see the Supporting Information), and is

$$T_c = (KS(S+1) + [K^2[S(S+1)]^2 + 72J^2S(S+1)S'(S'+1)]^{1/2}) / (6k_B) \quad (4)$$

where  $J$  is the coupling within the layers between the low-spin  $\text{Mn}^{\text{II}}$  ( $z = 6$  for the six high-spin nearest neighbors) with spin  $S$ , and the high-spin  $\text{Mn}^{\text{II}}$  ( $z = 4$  for the three high-spin and one low-spin nearest neighbors) with  $S'$ , and  $K$  is the interlayer coupling between adjacent high-spin  $\text{Mn}^{\text{II}}$  ( $z = 4$ ) sites.

A summary of the MF equations for general spin for the aforementioned cases 1 to 3 is contained in Table 2.

## ESTIMATION OF EXCHANGE COUPLING, $J$

Based on a  $T_c$  of 78 K, the exchange coupling,  $J$ , for  $\text{M}(\text{CN})_2$  (3) is estimated from eq 1 as  $J/k_B$  is  $-6.7$  K that is in accord with antiferromagnetic coupling. For the layered ferrimagnet  $[\text{NEt}_4]_2\text{Mn}^{\text{II}}_3(\text{CN})_8$ , eq 3 gives an antiferromagnetic coupling between adjacent  $\text{Mn}^{\text{II}}$  sites of  $J/k_B = -7.1$  K. The  $-6.7$  and  $-7.1$  K agree well, as expected for the same  $\text{Mn}^{\text{II}}-\text{C}\equiv\text{N}-\text{Mn}^{\text{II}}$  linkages, albeit for  $[\text{NEt}_4]_2\text{Mn}^{\text{II}}_3(\text{CN})_8$  the C-bonded  $\text{Mn}^{\text{II}}$  is low spin ( $S = 1/2$ ), while it is high spin ( $S = 5/2$ ) for  $\text{M}(\text{CN})_2$ .<sup>9,15</sup> The slightly reduced  $J$  for  $\text{Mn}^{\text{II}}\text{CNMn}^{\text{II}}$  when both  $\text{Mn}^{\text{II}}$  sites are tetrahedral and high spin with respect to when the  $\text{Mn}^{\text{II}}-\text{C}$  site is octahedral and low spin is in accord with the slightly longer ( $\sim 0.2$  Å)  $\text{Mn}^{\text{II}}\cdots\text{Mn}^{\text{II}}$  separation (Table 1).<sup>10</sup>

The intralayer,  $J$ , and interlayer,  $K$ , exchange coupling for  $[\text{NEt}_4]\text{Mn}^{\text{II}}_3(\text{CN})_7$  (2) can be estimated from eq 4. However, only  $T_c$  is known, thus,  $J$  and  $K$  cannot be independently determined. Since  $[\text{NEt}_4]\text{Mn}^{\text{II}}_3(\text{CN})_7$  and  $[\text{NEt}_4]_2\text{Mn}^{\text{II}}_3(\text{CN})_8$  possess virtually identical 2-D layers, the interlayer coupling constant,  $K$ , can be estimated by assuming the value for  $J$  calculated for  $[\text{NEt}_4]_2\text{Mn}^{\text{II}}_3(\text{CN})_8$  using eq 3, that is,  $-7.1$  K. This is a good assumption, as both  $[\text{NEt}_4]\text{Mn}^{\text{II}}_3(\text{CN})_7$  and  $[\text{NEt}_4]_2\text{Mn}^{\text{II}}_3(\text{CN})_8$  have identical layers with the same linkages and the identical spin states for each  $\text{Mn}^{\text{II}}$  ion, but due to the terminal cyanides, cations, and solvents separating the layers for  $[\text{NEt}_4]_2\text{Mn}^{\text{II}}_3(\text{CN})_8$ , the isolated layers are nonbridging. Thus, its intralayer coupling  $K$  is negligible and is assumed to be zero. Using the estimated value  $J/k_B = -7.1$  K and  $T_c = 28.5$  K, the interlayer coupling,  $K/k_B$ , between the tetrahedral high-spin  $\text{Mn}^{\text{II}}$  ions via superexchange in  $[\text{NEt}_4]\text{Mn}^{\text{II}}_3(\text{CN})_7$  is estimated as  $-1.8$  K. Alternatively, the interlayer coupling,  $K$ , between the tetrahedral high-spin  $\text{Mn}^{\text{II}}$  ions can also be assumed to be similar to the intralattice coupling calculated for  $\text{Mn}(\text{CN})_2$ , that is,  $-6.7$  K, and based on this and the  $T_c$ ,  $J/k_B$  is  $-4.4$  K. The negative  $K$  indicates antiferromagnetic coupling between the ferrimagnetic layers, which is observed.

Note that  $K$  can be estimated from the critical field,  $H_c \{= |K| S^2 / [\mu_B(S - S')]\}$ , for the spin-flop transition.<sup>16</sup> Since the spin flop transition is not observed<sup>8</sup> up to 9 T,  $|K|/k_B > 3.8$  K, which is consistent with the estimate of  $K/k_B = -6.7$  K above. The spin-flop field for that value of  $K$  would be  $\sim 14$  T.

The value of  $K$  should be comparable to both  $J$  for  $[\text{NEt}_4]_2\text{Mn}^{\text{II}}_3(\text{CN})_8$  as well as  $\text{Mn}(\text{CN})_2$ , as the linkages are comparable. This is observed as  $K/J_{\text{Mn}_3(\text{CN})_8} = 0.25$ , and  $K/J_{\text{Mn}(\text{CN})_2} = 0.66$ . The disparity in these ratios is within reason, as MF Theory does not attempt to incorporate any interlattice coupling for  $\text{Mn}(\text{CN})_2$  due to the absence of interlattice bonding.

Similar to tetrahedral  $\text{Mn}(\text{CN})_2$ , cubic PBAs have only one type of exchange coupling,  $J$ , and thus  $\text{Mn}(\text{CN})_2$  can be compared to  $J$  values estimated from a MF analysis of PBAs based on octahedral metal ion sites. Cubic and distorted cubic PBAs have one  $J$ ; however, the M bound to the cyanide carbon may differ from the M' bound to the nitrogen carbon. Equation 2 is the result of the MF analysis for this structure. For a similar reason the  $J$  values for  $[\text{NEt}_4]_2\text{Mn}^{\text{II}}_3(\text{CN})_8$  and  $[\text{NEt}_4]\text{Mn}^{\text{II}}_3(\text{CN})_7$  can be assessed. Hence, a comparison of  $J$  values, which are independent of both  $S$  and  $z$ , can be made. MF Theory applied to the known cubic  $\text{AMn}^x[\text{Mn}^y(\text{CN})_6]$  PBA materials yield  $J/k_B$  between 3.5  $\{\text{CsMn}^{\text{II}}[\text{Mn}^{\text{III}}(\text{CN})_6]^{17}\}$  and 8.7 K  $\{\text{Mn}^{\text{III}}_3[\text{Mn}^{\text{II}}(\text{CN})_6]_2^{18}\}$  using eq 2. Likewise, eq 2 can be



Table 3. Summary of Representative Coupling Constants,  $J$ , for Mn-Based PBAs etc. Possessing M–CN–M' Linkages, Using eq 2<sup>a</sup>

PBA	MCNM, Å	$T_c$ , K	$S_M$	$S_{M'}$	$J/k_B$ , K	ref
CsMn <sup>II</sup> [Mn <sup>III</sup> (CN) <sub>6</sub> ] <sub>2</sub> ·1/2H <sub>2</sub> O	5.33 <sup>b</sup>	29 31	1	5/2	3.47	18
	5.35 <sup>b</sup>				3.71	15
Mn <sup>II</sup> [Mn <sup>IV</sup> (CN) <sub>6</sub> ]	5.37 <sup>b</sup>	48.7	3/2	5/2	4.28	19
Mn <sup>III</sup> [Mn <sup>III</sup> (CN) <sub>6</sub> ]	5.33 <sup>b</sup>	31	1	2	4.47	20
Mn <sup>III</sup> <sub>3</sub> [Mn <sup>II</sup> (CN) <sub>6</sub> ] <sub>2</sub> ·2H <sub>2</sub> O	5.31 <sup>b</sup>	37	1/2	2	8.72	16
CsNi <sup>II</sup> [Cr <sup>III</sup> (CN) <sub>6</sub> ] <sub>2</sub> ·2H <sub>2</sub> O	5.29 <sup>b</sup>	90	3/2	1	16.4	21
Na <sub>2</sub> Mn <sup>II</sup> [Mn <sup>II</sup> (CN) <sub>6</sub> ] <sub>2</sub> ·2H <sub>2</sub> O	5.33	31	5/2	1/2	6.05	6
Na <sub>2</sub> Mn <sup>II</sup> [Mn <sup>II</sup> (CN) <sub>6</sub> ]	4.99	57	5/2	1/2	11.1	6
K <sub>2</sub> Mn <sup>II</sup> [Mn <sup>II</sup> (CN) <sub>6</sub> ]	5.09	41	5/2	1/2	8.00	5, 16
Rb <sub>2</sub> Mn <sup>II</sup> [Mn <sup>II</sup> (CN) <sub>6</sub> ]	5.19	34.6	5/2	1/2	6.75	5
Cs <sub>2</sub> Mn <sup>II</sup> [Mn <sup>II</sup> (CN) <sub>6</sub> ]	5.31 <sup>b</sup>	21	5/2	1/2	4.10	5
KV <sup>II</sup> Cr <sup>III</sup> (CN) <sub>6</sub> ]	5.28 <sup>b</sup>	376	3/2	3/2	50.1	3
Cs <sub>2</sub> Mn <sup>II</sup> [V <sup>II</sup> (CN) <sub>6</sub> ]	5.33 <sup>b</sup>	125	5/2	3/2	10.9	22
CsMn <sup>II</sup> [Cr <sup>III</sup> (CN) <sub>6</sub> ]	5.41 <sup>b</sup>	90	5/2	3/2	7.86	23
CsNi <sup>II</sup> [Cr <sup>III</sup> (CN) <sub>6</sub> ] <sub>z</sub> ·zH <sub>2</sub> O ( $z = 3 \pm 1$ )	5.29	42	1	1	10.5	16
V <sup>III</sup> [Mn <sup>III</sup> (CN) <sub>6</sub> ]	4.65	28	3/2	1	5.11	20
Cr <sup>III</sup> [Mn <sup>III</sup> (CN) <sub>6</sub> ]	5.29 <sup>b</sup>	22	3/2	1	4.02	20

<sup>a</sup> $z_M = z_{M'} = 6$ . <sup>b</sup> $a/2$ .

used for the distorted cubic A<sub>2</sub>Mn[Mn(CN)<sub>6</sub>] (A = Na, K, Rb),<sup>5,6</sup> as the lattice connectivity is the same, and  $J/k_B$  ranges from 6.05 to 11.1 K (Table 2). The couplings for these Mn–CN–Mn systems are an order of magnitude lower than those for PBs containing V, Ni, and Cr, which have  $T_c$  values of an order of magnitude larger, Table 3.<sup>2c,19</sup>

## CONCLUSION

General spin,  $S$ , MF expressions for several 2- and 3-D noncubic Prussian Blue analogues were presented that relate the exchange constants and the critical temperature,  $T_c$  and the inter- and intralayer coupling constants for various noncubic PBAs compounds using these expressions were evaluated. The sign of the inter- and intralayer coupling constants for compounds studied indicate antiferromagnetic coupling, as observed. The  $K/J_{Mn_3(CN)_8} = 0.25$ , and  $K/J_{Mn(CN)_2} = 0.66$  ratios match reasonably, but not quantitatively. The application of MFT to several cubic PBAs produced coupling values with a smaller deviation in coupling value, as expected for changing only spin states. Examination of noncubic PBAs found the expected inverse relationship between coupling strength and spin site distance, and MFT proves to be most useful in the comparative analysis of magnetic coupling in structurally related compounds.

## ASSOCIATED CONTENT

### Supporting Information

The derivation of the MF expressions for the simple Heisenberg model for compounds 1 and 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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