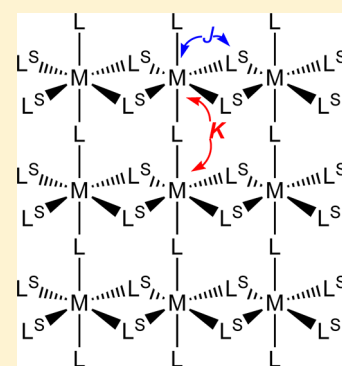


Mean Field Analysis of the Exchange Coupling (J) for Two- and Three-Dimensional Structured Tetracyanoethenide ($\text{TCNE}^{\bullet-}$)-Based Magnets

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Supporting Information

ABSTRACT: Mean field expressions based on the simple Heisenberg model were derived to correlate the inter- and intralayer exchange couplings to the critical temperatures, T_c , for several tetracyanoethylene (TCNE)-based magnets with extended two- and three-dimensional (2-D and 3-D) structure types. These expressions were used to estimate the exchange coupling, J , for 2-D ferrimagnetic $[\text{M}^{\text{II}}(\text{TCNE})(\text{NCMe})_2]^+$ ($\text{M} = \text{Mn}, \text{Fe}$), 3-D antiferromagnetic $\text{Mn}^{\text{II}}(\text{TCNE})[\text{C}_4(\text{CN})_8]_{1/2}$, and 3-D ferrimagnetic $\text{Mn}^{\text{II}}(\text{TCNE})_{3/2}(\text{I}_3)_{1/2}$. The type and magnitude of the exchange coupling are in accord with the previously reported magnetic data.



INTRODUCTION

Several organic-based magnets^{1–3} with tetracyanoethylene in its monoreduced form, $[\text{TCNE}]^{\bullet-}$,⁴ have been reported.³ Their structures, based on the perspective of extended bonding, span from isolated, ionic $[\text{TCNE}]^{\bullet-}$ [zero-dimensional (0-D) extended bonding] to three-dimensional (3-D) extended network structures, possessing $\mu_4^-[\text{TCNE}]^{\bullet-}$. Examples possessing manganese cations include 0-D $[\text{Mn}^{\text{III}}(\text{C}_5\text{Me}_5)_2]^+[\text{TCNE}]^{\bullet-}$,⁵ one-dimensional (1-D) $[\text{Mn}^{\text{III}}\text{TTP}]^+[\text{TCNE}]^{\bullet-}$,⁶ two-dimensional (2-D) $\text{Mn}^{\text{II}}(\text{TCNE})\text{I}(\text{OH})_2$,⁷ and 3-D $\text{Mn}^{\text{II}}(\text{TCNE})_{3/2}(\text{I}_3)_{1/2}$.⁸ The family member with the highest magnetic ordering temperature, T_c , which exceeds room temperature, is $\text{V}[\text{TCNE}]_x$.⁹ It is, however, amorphous, and its structure has been elusive, although it is proposed to be 3-D.¹⁰ In addition to these examples, other structurally characterized have been reported.^{8,11–15}

Prototype 2-D and 3-D structured TCNE-based magnetic materials are (a) $[\text{Fe}^{\text{II}}(\text{TCNE})(\text{NCMe})_2][\text{FeCl}_4]$ ¹¹ (Figure 1) and $[\text{M}^{\text{II}}(\text{TCNE})(\text{NCMe})_2][\text{SbF}_6]$ ($\text{M} = \text{Mn}, \text{Fe}$)¹² that possess $S = 1/2 \mu_4^-[\text{TCNE}]^{\bullet-}$ extended network bonding in 2-D; (b) $\text{M}^{\text{II}}(\text{TCNE})[\text{C}_4(\text{CN})_8]_{1/2} \cdot z\text{CH}_2\text{Cl}_2$ ($\text{M} = \text{Mn}, \text{Fe}$)¹⁵ that possesses extended network bonding in 2-D via $S = 1/2 \mu_4^-[\text{TCNE}]^{\bullet-}$ in which these layers are bridged by $S = 0 \mu_4^-[\text{C}_4(\text{CN})_8]^{2-}$, that is, extended network bonding in 3-D; and (c) $\text{Mn}^{\text{II}}(\text{TCNE})_{3/2}(\text{I}_3)_{1/2} \cdot z\text{THF}$ ⁸ that possesses extended network bonding in 3-D via $S = 1/2 \mu_4^-[\text{TCNE}]^{\bullet-}$ (Figure 3). The T_c ranges from 67 to 171 K, Table 1.

Each of these 2-D and 3-D organic-based magnets possesses $S = 1/2 \mu_4^-[\text{TCNE}]^{\bullet-}$ that is bonded to and antiferromagnetically coupled to four high spin M^{II} ions ($S = 5/2 \text{Mn}^{\text{II}}$,

$S = 2 \text{Fe}^{\text{II}}$) by direct exchange. This leads to extended, nonfrustrated antiferromagnetically coupled layers. As a consequence, the 2-D structured magnets order as ferrimagnets.^{11,12} $\text{Mn}^{\text{II}}(\text{TCNE})_{3/2}(\text{I}_3)_{1/2} \cdot z\text{THF}$ has an additional $S = 1/2 \mu_4^-[\text{TCNE}]^{\bullet-}$ linking the layers. It also bonds to and antiferromagnetically couples to the $S = 5/2 \text{Mn}^{\text{II}}$ ions leading to extended 3-D, nonfrustrated antiferromagnetic coupling within and between layers, and ordering as a ferrimagnet.⁸

$\text{M}(\text{TCNE})[\text{C}_4(\text{CN})_8]_{1/2}$ has the same layered structure and magnetic coupling, but the layers are linked via $S = 0 \mu_4^-[\text{C}_4(\text{CN})_8]^{2-}$. Consequently, $\text{M}(\text{TCNE})[\text{C}_4(\text{CN})_8]_{1/2}$ has a 3-D extended network structure. This diamagnetic $[\text{C}_4(\text{CN})_8]^{2-}$ anion provides a conjugated, 5-atom $-\text{N}\equiv\text{C}-\text{C}-\text{C}\equiv\text{N}$ -superexchange path that antiferromagnetically couples the ferrimagnetic layers, stabilizing an antiferromagnetic ground state. Because of Fe^{II} being anisotropic, the magnetic ground state has more complex magnetic behavior including metamagnetism and canting is observed.¹⁶

An important aspect of understanding organic-based magnets and enhancing their transition temperatures is the identification of the nearest neighbor exchange coupling, J , for these magnetic materials. The mean field (MF) approximation to the Heisenberg model $[H = -\sum_{ij} J_{ij} S_i \cdot S_j \text{ (} i > j \text{)}]$,¹⁷ eq 1, has been used extensively to relate T_c with an average J . This expression is applicable for isotropic materials with one type of spin site of total spin, S , where z is the number of nearest neighbors, and k_B

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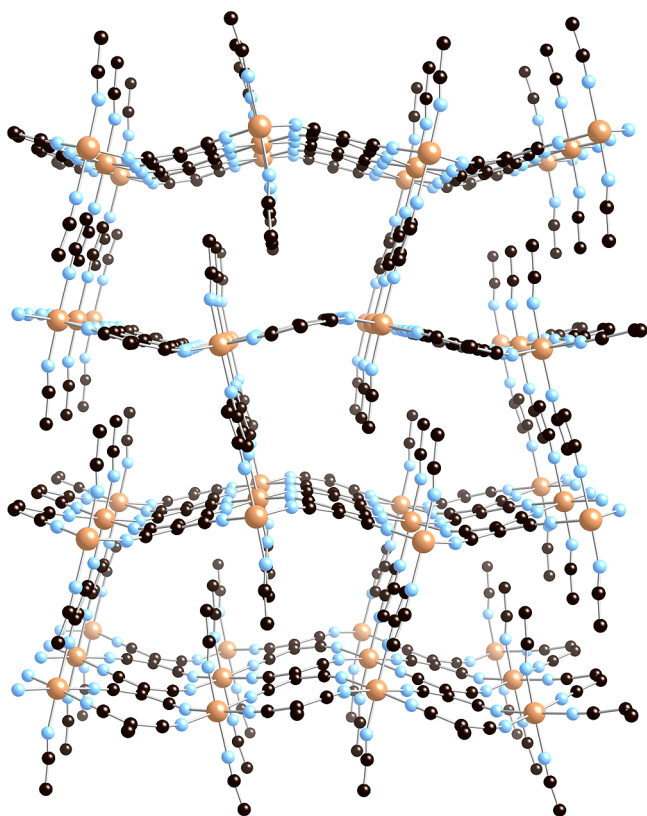


Figure 1. 2-D Extended network bonding via μ_4 -[TCNE] $^{*+}$ observed for $[\text{Fe}^{\text{II}}(\text{TCNE})(\text{NCMe})_2]^+$ in $[\text{Fe}^{\text{II}}(\text{TCNE})(\text{NCMe})_2][\text{FeCl}_4]$ (**1c**) (Fe = gold; C = black, N = blue).¹¹ The ordered anions reside in the channels (structure type A *vide infra*).

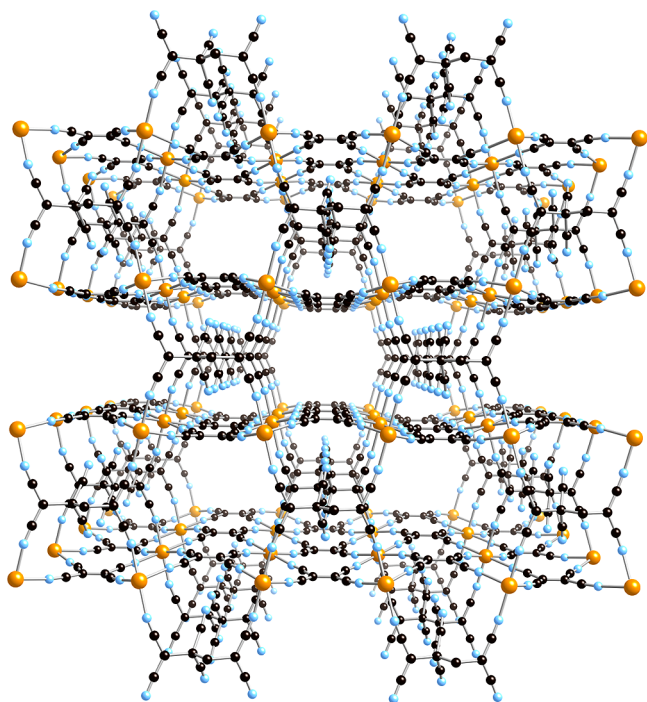


Figure 2. 3-D Extended network bonding via 2-D μ_4 -[TCNE] $^{*+}$ in which these layers are bridged by μ_4 -[C₄(CN)₈] $^{2-}$ that is reported for $\text{M}^{\text{II}}(\text{TCNE})[\text{C}_4(\text{CN})_8]_{1/2} \cdot z\text{CH}_2\text{Cl}_2$ (M = Mn,⁸ Fe¹⁵) (**2**) (M = gold; C = black, N = blue). The disordered solvent resides in the channels (structure type B *vide infra*).

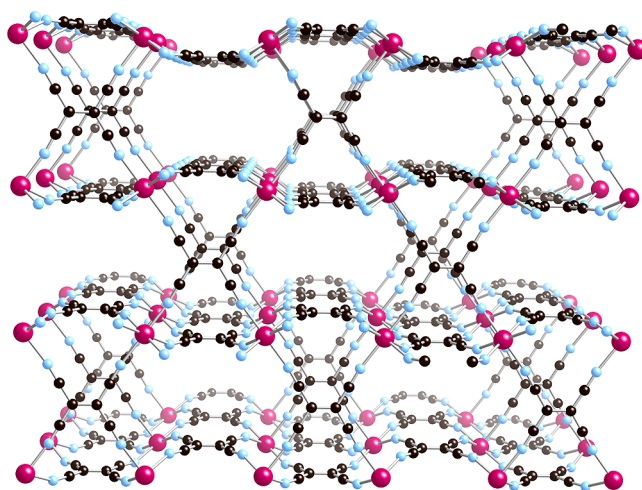


Figure 3. Extended network bonding via μ_4 -[TCNE] $^{*+}$ in 3-D present for $\text{Mn}^{\text{II}}(\text{TCNE})_{3/2}(\text{I}_3)_{1/2} \cdot z\text{THF}$ (**3**) (Mn = red; C = black, N = blue).⁸ The ordered solvent and ordered I_3^- anion resides in the channels (structure type C₂ *vide infra*).

is the Boltzmann's constant. For antiferromagnetic systems $|J| = -J$ will be used.¹⁷

As MF theory ignores the effect of topology (i.e., dimensionality) on T_c , it gives the same result for any material with the same spin species, exchange coefficients, and bonding, regardless of the system dimension. MF theory also gives the same result for either Heisenberg or Ising spins (confined to a single axis). In the absence of anisotropy, however, long-range spin fluctuations will destroy the magnetic order of a 1-D or 2-D system (Mermin–Wagner theorem).¹⁷ By evaluating the spin excitation spectrum of a 2-D system with exchange, J , Erickson and Mills discovered that the transition temperature rises very rapidly with easy-axis anisotropy D with $T_c \sim J/\log(J/D)$.¹⁸ Thus, MF theory can provide an adequate approximation for an anisotropic 2-D material when $D/J \gg 1$. If D is not large compared to J , the transition temperature of a 2-D material will be suppressed by long-range fluctuations and higher T_c 's will occur when the effect of those fluctuations is diminished by 3-D magnetic order. But even for a 3-D system, MF theory may still overestimate the transition temperature by as much as 40%. Therefore, MF theory is best used to estimate the ratios of exchange constants either for different materials or within the same material.

The MF expression for an isotropic system possessing two different spin sites, i and j , has also been developed, eq 2,^{17,19} where z_i and z_j are the number of nearest neighbors, and S_i and S_j are the total spin on spin sites i and j , respectively, and the Landé g values for each spin site are the same.

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

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

While appropriate and providing insightful relations for cubic systems such as Prussian blue analogues,¹⁹ eq 2 is tenuous for noncubic TCNE-based organic-based magnets. With the initial goal to identify the exchange coupling within ($J = J_{\text{intra}}$) and between layers of 2-D and structurally bridged 2-D (3-D), as well as 3-D magnetic materials based their observed T_c an MF

Table 1. Summary of Structurally Characterized 2-D and 3-D TCNE-Based Magnets and Their T_c 's

magnet	interlayer separation, (Å)	bonding dimensionality	T_c^a (K)	type ^b	ref	
[Fe ^{II} (TCNE)(NCMe) ₂][FeCl ₄]	1c	8.24	2-D	90	FI	11
[Mn ^{II} (TCNE)(NCMe) ₂][SbF ₆]	1a	8.15	2-D	67	FI	12
[Fe ^{II} (TCNE)(NCMe) ₂][SbF ₆]	1b	8.14	2-D	96	FI	12
Mn ^{II} (TCNE)[C ₄ (CN) ₈] _{1/2} ·zCH ₂ Cl ₂	2	8.77	3-D	70	AF	8, 16
Fe ^{II} (TCNE)[C ₄ (CN) ₈] _{1/2} ·zCH ₂ Cl ₂		8.71	3-D	86	AF/MM	16
Mn ^{II} (TCNE) _{3/2} (I ₃) _{1/2} ·zTHF	3	7.96	3-D	169	FI	8

^aFrom the peak in $\chi'(T)$. ^bFI = ferrimagnet; AF = antiferromagnet; MM = metamagnetic behavior.

analysis was performed for the family of magnets described above and it is reported herein.

The T_c 's for materials discussed were determined in several ways with some variation between methods.^{8,11,12,16,20} To be self-consistent with our MF analysis, the same method, namely, the temperature at which the maxima in the frequency independent $\chi'(T)$ is used as T_c . These values are listed in Table 1.

MF theory is useful for predicting trends and for qualitative estimates of exchange constants. Although MF theory can overestimate T_c by as much as 40%,¹⁹ it provides better estimates for the ratios of exchange couplings in different materials. This paper uses MF theory to estimate the ratios of the interlayer and intralayer couplings (J/K or J/J').

The MF analysis for several 2-D and 3-D structure-types with general spin, S , led to the identification of expressions that relate the exchange couplings to T_c . These expressions are then evaluated using experimental data for 2-D layered [M(TCNE)(NCMe)₂][X] {M = Mn (1a), Fe (1b); X = [SbF₆]⁻; M = Fe, X = [Fe^{III}Cl₄]⁻ (1c)}, 3-D bridged Mn(TCNE)[C₄(CN)₈]_{1/2} (2), and 3-D Mn(TCNE)_{3/2}(I₃)_{1/2} (3) to estimate the values of their exchange couplings.

MEAN FIELD EXPRESSIONS

The MF expressions for T_c , using $H = -\sum_j J_{ij} S_i S_j$ ($i > j$), are determined for various structure-types: (A) 2-D layered system with two spin sites and intralayer coupling J ; (B) 3-D system with two spin sites and a diamagnetic bridging ligand with intralayer coupling, J , and interlayer metal ion to metal ion coupling, K ; (C₁ and D₁) 3-D system with three spin sites with intralayer J and interlayer metal ion to nonmetal J' couplings; and (C₂ and D₂) 3-D system with two spin sites and with isotropic exchange coupling, J . This paper adopts the sign convention that J , J' , or $K > 0$ correspond to ferromagnetic coupling.

Structure-Type A. The MF solution for the general spin case of a 2-D structure-type A material of M(L^S)(L^{NB})₂ (M = metal ion; L^S = spin bearing ligand; L^{NB} = nonspin bearing, nonbridging species) composition, Figure 4, was constructed. MF theory predicts

$$T_c = \frac{4}{3k_B} |J| \sqrt{S(S+1)S'(S'+1)} \quad (3)$$

where J is the coupling between M ($z = 4$) and L^S ($z = 4$) within the layers, $S =$ spin on M, and $S' =$ spin on L^S.

Structure-Type B. The MF expression for the general spin case for 3-D structure-type B material of M(L^S)(L) (L = nonspin bearing, bridging species) composition, Figure 5, is

$$T_c = \frac{1}{3k_B} [KS(S+1) + \sqrt{K^2[S(S+1)]^2 + 16J^2S(S+1)S'(S'+1)}] \quad (4)$$

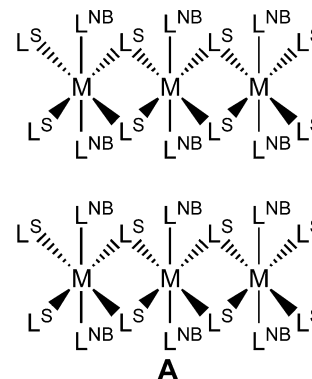


Figure 4. Generalized bonding scheme for 2-D layered compounds with formula M(L^S)(L^{NB})₂ of structure-type A.

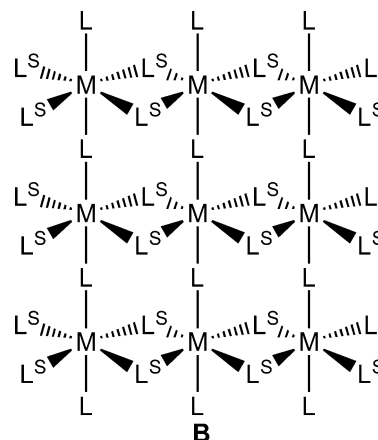


Figure 5. Generalized bonding scheme for compounds with formula M(L^S)(L) of structure type B.

where J is the intralayer coupling between M ($z = 4$) and L^S ($z = 4$), K is the interlayer coupling between M and M, $S =$ spin on M, and $S' =$ spin on L^S.

Structure-Type C. The MF expression for the general spin case for 3-D structure-type C₁ material of M(L^{S1})(L^{S2})_{1/2} [M = metal ion ($z = 6$); L^{S1} = spin bearing ligand ($z = 4$); L^{S2} = spin bearing species (different than L^{S1}) ($z = 4$)] composition, Figure 6a, is

$$T_c = \frac{2}{3k_B} \sqrt{S(S+1)[4J^2S'(S'+1) + 2J'^2S''(S''+1)]} \quad (5)$$

For three different spin species, a cubic equation generally results. But because certain spin interactions are missing, T_c is given by the quadratic expression 5. For the case of isotropic coupling ($J \sim J'$) and one spin bearing ligand (L^{S1} = L^{S2} = L^S ($z = 4$); $S' \sim S''$) of M(L^S)_{3/2} composition and structure-type C₂,

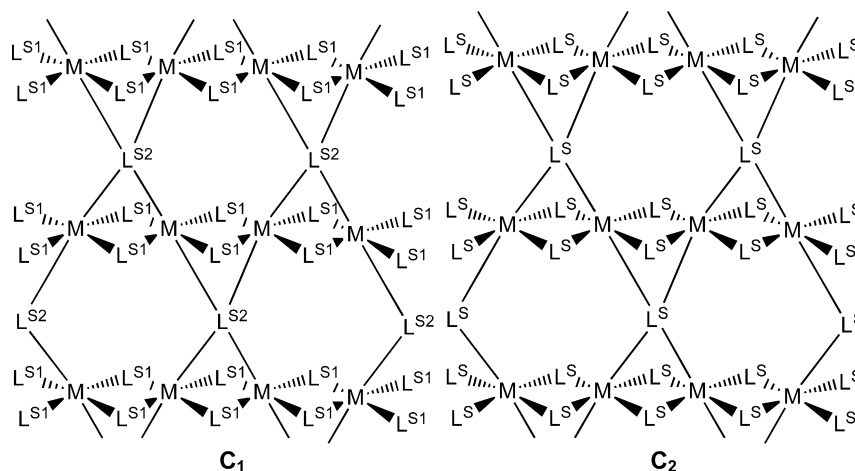


Figure 6. Generalized bonding schemes for $M(L^{S1})(L^{S2})_{1/2}$ of structure-type C_1 , and $M(L^S)_{3/2}$ of structure-type C_2 .

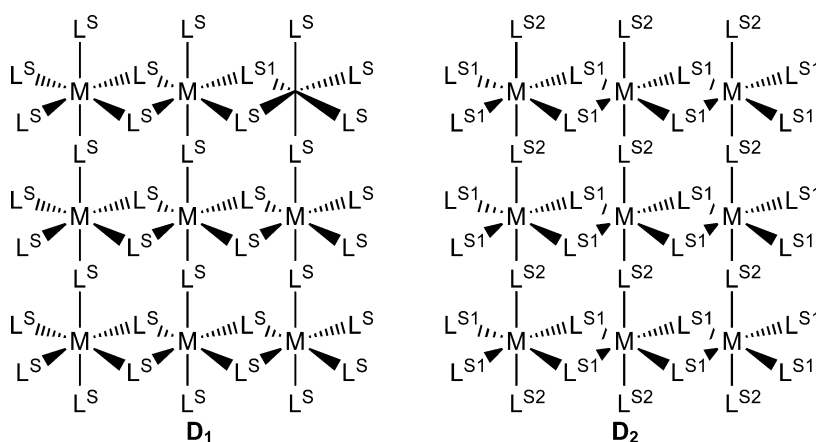


Figure 7. Generalized bonding scheme for $M(L^{S1})(L^{S2})$ of structure-type D_1 , and $M(L^S)_2$ of structure-type D_2 .

Figure 6b, eq 5 reduces to eq 6.

$$T_c = \frac{2}{3k_B} |J| \sqrt{6S(S+1)S'(S'+1)} \quad (6)$$

Structure-Type D. The MF expression for the general spin case for 3-D structure-type D_1 material of $M(L^{S1})(L^{S2})$ [M = metal ion ($z = 6$); L^{S1} = spin bearing ligand ($z = 4$); L^{S2} = spin bearing species (different than L^{S1}) ($z = 2$)] composition, Figure 7, is

$$T_c = \frac{2}{3k_B} \sqrt{S(S+1)[4J^2S'(S'+1) + J'^2S''(S''+1)]} \quad (7)$$

Once again, T_c is given by a quadratic expression, as shown in the Supporting Information.

For the case of isotropic coupling ($J \sim J'$), for a material with $S' = S''$, $M(L^S)_2$ composition, and structure-type D_2 , Figure 7b, eq 7 reduces to eq 8. Note that this situation is unlikely as the coordination environment for L^{S1} and L^{S2} are different; thus, $J \sim J'$ is likewise unlikely. Nonetheless, it is useful for comparison purposes.

$$T_c = \frac{2}{3k_B} |J| \sqrt{5S(S+1)S'(S'+1)} \quad (8)$$

The difference in T_c 's between structure-type C_2 and hypothetical structure-type D_2 , assuming the identical spins and

$J(C_2) \sim J(D_2)$ can be calculated eq 9, and the ratio is 1.1. Thus, a 10% enhancement of T_c is expected if the bridging ligand goes from $z = 2$ to $z = 4$, that is, magnets with structure C_2 should have a 10% higher T_c with respect to those with structure D_2 for the metal ions, S , and S' , or conversely a 10% reduced J would be needed for the same T_c .

$$\frac{T_c(C_2)}{T_c(D_2)} = \frac{J(C_2)}{J(D_2)} \sqrt{\frac{6}{5}} = 1.1 \frac{J(C_2)}{J(D_2)} \quad (9)$$

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

Estimation of Exchange Coupling, J . The exchange coupling, J , for 1a, 1b, and 1c of structure-type A [$M = Mn^{II}$ (1a); Fe^{II} (1b, 1c), $L^S = \mu_4^-[\text{TCNE}]^{\bullet-}$; $L^{NB} = \text{NCMe}$; $S = 5/2$ (1a) or 2 (1b, 1c) and $S' = 1/2$], can be estimated from eq 3. On the basis of previously reported values for T_c of 67, 96, and 90 K for 1a, 1b, and 1c, J/k_B is estimated as -19.6 , -33.9 , and -31.8 K, respectively. These values are identical to those obtained by using the classical MF expression, eq 2, for a two-spin system (or lattice) with an isotropic J . Upon the basis of the aforementioned convention, the negative J indicates antiferromagnetic coupling between M^{II} and $\mu_4^-[\text{TCNE}]^{\bullet-}$ for these three 2-D compounds producing ferrimagnetic layers. This agrees with previously reported experimental data.^{11,12}

The intralayer, J , and interlayer, K , coupling constants for 2 of structure-type B ($M = Mn^{II}$, $L^S = \mu_4^-[\text{TCNE}]^{\bullet-}$,

Table 2. Summary of MF Expressions [$H = -\sum J_{ij} S_i^z S_j^z$ ($i > j$)] for general S for 2-D and 3-D structure types A, B, C₁, C₂, and D

Formula ^a (structure-type)	Mean Field Expression for T_c ^b
2-D	
$M(L^S)(L^{NB})_2$ (A)	$T_c = \frac{4}{3k_B} J \sqrt{S(S+1)S'(S'+1)}$
3-D	
$M(L^S)(L)$ (B)	$T_c = \frac{1}{3k_B} [KS(S+1) + \sqrt{K^2[S(S+1)]^2 + 16J^2S(S+1)S'(S'+1)}]$
$M(L^{S1})(L^{S2})_{1/2}$ (C ₁)	$T_c = \frac{2}{3k_B} \sqrt{S(S+1)[4J^2S'(S'+1) + 2J'^2S'(S'+1)]}$
$M(L^S)_{3/2}$ (C ₂)	$T_c = \frac{2}{3k_B} J \sqrt{6S(S+1)S'(S'+1)}$
$M(L^{S1})(L^{S2})$ (D ₁)	$T_c = \frac{2}{3k_B} \sqrt{S(S+1)[4J^2S'(S'+1) + J'^2S'(S'+1)]}$
$M(L^S)_2$ (D ₂)	$T_c = \frac{2}{3k_B} J \sqrt{5S(S+1)S'(S'+1)}$

^aM = metal ion; L^S, L^{S1}, and L^{S2} = spin bearing species; L^{NB} = nonspin bearing, nonbridging species. L = non-spin bearing, bridging species.
^bJ = intralayer coupling between M and L^S or L^{S1}; K = interlayer M and M coupling; J' = interlayer M and L^{S2} coupling; S = spin on M; S' = spin on L^S or L^{S1}; S'' = spin on L^{S2}.

$L = [C_4(CN)_8]^{2-}$; $S = 5/2$, $S' = 1/2$), can be estimated from eq 4. Because only T_c is known, J and K cannot be solved individually. Since **1a** and **2** possess similar 2-D layers, however, the interlayer coupling constant, K , can be estimated by assuming the value for J calculated for **1a** using eq 3. This is a reasonable assumption, as both **1a** and **2** possess corrugated sheets of Mn^{II} ions coordinated to four μ_4 -[TCNE]^{•-} anions, but due to the *trans* acetonitrile ligands for **1a**, the nonbridging layers are isolated, and the intralayer coupling K is negligible and assumed to be zero. The value of T_c for **2** can vary depending on the method used to obtain it; therefore, the value of K/k_B will also vary. As noted earlier, for self-consistency, the temperature at which the maxima in the $\chi'(T)$ occurs is T_c , that is, 70 K. Thus, $J/k_B = -19.6$ K and the interlayer coupling, K/k_B , between the Mn^{II} ions via superexchange in **2** is estimated as -1.02 K.

Again using the aforementioned convention, the negative K indicates antiferromagnetic coupling between the ferrimagnetic layers, as expected. This coupling is much weaker than the intralayer coupling, J , by a factor of 20. The antiferromagnetic coupling between the ferrimagnetic layers produces an antiferromagnetic ground state. K can also be estimated from the 19.5 kOe critical field for its spin-flip transition,¹⁶ which gives an experimental interlayer exchange value, K/k_B , of -0.42 K.²¹ Using eq 4, the K obtained from the spin-flip transition, and the estimated $J/k_B = -19.6$ K from **1a**, T_c is 68.2 K. Thus, an interlayer coupling of -0.42 K leads to an increase in T_c of 1.2 K. Although K obtained via MF theory is in good agreement, it may be overestimated by a factor of 1.5 (the range of error for a MF analysis).

Mn(TCNE)I(OH₂)⁷ also has the A structure {M = Mn^{II}, L^S = μ_4 -[TCNE]^{•-}, L^{NB} = I, OH₂}. However, a MF analysis of the exchange coupling, J , is inappropriate as the T_c of 171 K is (a) double that for other structure A materials, and is (b) the same as compound **3** that has extended 3-D (C₂) bonding. Furthermore, the 5.00 Å interlayer separation is substantially reduced (>35%) from the ≥ 8.0 Å interlayer separation for the other type A materials, suggesting stronger interlayer coupling. Also, the dissymmetric bonding of the μ_4 -[TCNE]^{•-} in Mn(TCNE)I(OH₂) differs from that observed for other type A materials. Since the ground state is not antiferromagnetic, it must be ferrimagnetic, perhaps dipolar in origin, which can be substantial for layered systems.²² Hence, the interlayer

coupling, K , cannot be neglected for Mn(TCNE)I(OH₂) as was done for the other compounds with this structure-type A, and the MF analysis is not appropriate.

Because of the more complex magnetic behavior of Fe(TCNE)[C₄(CN)₈]_{1/2} (analogous to **2**), the coupling could not be estimated for this compound; that is, the magnetic behavior is more complicated than MF theory can predict. All forms of MF expressions have $T_c \propto S(S+1)$. Hence, T_c should be higher for $S = 5/2$ Mn^{II} with respect to $S = 2$ Fe^{II} by a factor of 1.46 for identical J values. Hence, the Mn^{II} analogue should have a T_c that exceeds the related Fe^{II} analogue. Since the Mn^{II} analogue has a lower T_c than the anisotropic Fe^{II} analogue, however, a larger $|J|$ must occur for the anisotropic Fe^{II} system and is perhaps attributable to $g \gg 2$. Likewise, the observed trend occurs for the anisotropic $S = 1/2$ Fe^{III} ($T_c = 4.8$ K)²³ and $S = 1$ Mn^{III} ($T_c = 8.8$ K)⁵ analogues of [M(C₅Me₅)₂]⁺[TCNE]^{•-} that have T_c 's that exceed the 3.65 K for the isotropic $S = 3/2$ Cr^{III} analogue.¹⁴ This trend is also noted for 3-D M[N(CN)₂]₂ (M = Cr, Mn, Fe, Co, Ni).²⁴ As discussed in the introduction, a MF comparison between anisotropic and isotropic systems is problematic because long-range spin fluctuations are suppressed in an anisotropic system, thereby elevating its transition temperature with respect to a similar isotropic system.

The structure of **3** has similar 2-D corrugated layers present for **1a** and **2**. In addition, it contains μ_4 -[TCNE]^{•-} ions that bridge the layers through the axial Mn^{II} ions, thereby creating a 3-D network structure with each $S = 5/2$ Mn^{II} bonded to six $S = 1/2$ μ_4 -[TCNE]^{•-}s. As a first approximation, the interlayer exchange coupling J' for **3** of structure-type C₁ {M = Mn^{II}, L^{S1} = μ_4 -[TCNE]^{•-} within the layers, and L^{S2} = μ_4 -[TCNE]^{•-} between the layers, and $S = 5/2$, $S' = 1/2$, and $S'' = 1/2$ }, can be estimated by using eq 5. Again, as only T_c is known, J and J' cannot be individually solved from this expression. However, using the same methodology that was used for **2**, the intralayer coupling J for **3** can be estimated by assuming the value that was calculated for **1a** using eq 3. This is reasonable as the structures of **1a** and **3** both possess similar 2-D ferrimagnetic layers. Unfortunately, this procedure gives $J'/k_B = -64.2$ K, which clearly overestimates $|J'|$. A more detailed comparison of the three structures revealed that the 2-D layers of **1a** and **3** significantly differ with respect to the corrugation. This is evident from the \angle Mn–N–C of all three compounds; that is,

the $\angle\text{Mn-N-C}$ are 169.2° , 174.3° , and 156.5° for **1a**, **2**, and **3**, respectively. This different buckling angles may create different couplings within the layers for **3** invalidating the assumption that $J(\mathbf{1a}) \sim J(\mathbf{3})$.

A more reasonable approach for **3** is to assume that the intralayer coupling is comparable to the interlayer coupling, that is, $J \sim J'$.⁸ Thus, the coupling for **3** can be estimated using eq 6 for general structure-type C_2 $\{\text{M} = \text{Mn}^{\text{II}}, L^S = \mu_4^- [\text{TCNE}]^{\bullet-}; \text{ and } S = 5/2, \text{ and } S' = 1/2\}$ and using the observed T_c of 169 K, $J/k_B = -40.4$ K. This is identical to that obtained by using the simplified MF expression, eq 2 for a two-spin system with an isotropic J . Thus, **3** with structure C_2 has approximately double the exchange coupling that was calculated for **1a** with structure **A**. On the other hand, the coupling of **3** should be around ~ 1.5 times that of **1a** based on the coordination environment. Albeit in the range of error for a MF analysis, the larger value may be due to differences in the corrugation and $\angle\text{Mn-N-C}$ that leads to enhanced coupling.

It should be noted that the antiferromagnetic exchange coupling for $\text{Mn}^{\text{III}}-\mu_4^-[\text{TCNE}]^{\bullet-}$ has been reported to be as high as several hundred Kelvin for the $[\text{Mn}^{\text{III}}(\text{TPP})]^+[\text{TCNE}]^{\bullet-}$ (TPP = *meso*-tetraphenylporphyrinato) family of organic-based magnets that have T_c 's up to 28 K,^{25,26} but these values were not determined from a MF analysis, and thus they cannot be directly compared to the MF results reported herein.

For comparison purposes, J/k_B of -146 K was calculated for the amorphous room temperature $V(\text{TCNE})_x$ using eq 6 and the previously reported T_c of 400 K.^{3,9} Since the coordination environment is unknown, it was assumed to be C_2 ($\text{M} = \text{V}^{\text{II}}, S = 3/2; L^S = \text{TCNE}, S' = 1/2$). This agrees with the value of -100 K from an analysis of the of the temperature dependence of the saturation magnetization by the Bloch law for spin wave theory.²⁷ Hence, the coupling for $V-[\text{TCNE}]^{\bullet-}$ is stronger as all of the reported high-temperature ($>$ room temperature) organic-based magnets are V-based.^{3,9,27-33} Although there are no known metal-TCNE compounds of structure type D_1 or D_2 , it has been proposed as a possible structure for $V(\text{TCNE})_x$.¹⁰ If structure D_1 is assumed the intralayer coupling, J , and interlayer coupling, J' , could not be estimated for $V(\text{TCNE})_x$ since only the T_c is known, and there are no comparable 2-D V-TCNE

structures in order to estimate the intralayer coupling. Nonetheless, assuming $V(\text{TCNE})_2$ has structure D_2 , then MF predicts J/k_B of -160 K, from eq 8. This is comparable to the exchange coupling value obtained of J/k_B of -100 K, from a previously reported method using Bloch law.²⁷

A summary of the exchange couplings for compounds **1-3** and $V(\text{TCNE})_x$ is presented in Table 3.

CONCLUSION

General spin, S , MF expressions for several 2-D and 3-D structure-types were presented that relate the exchange constants and the critical temperature, T_c . The inter- and intralayer coupling constants for various noncubic M^{II} -TCNE compounds using these expressions were evaluated. The sign of the inter- and intracoupling constants for compounds studied indicates antiferromagnetic coupling, as observed. For layered $[\text{M}(\text{TCNE})(\text{NCMe})_2]^+$ ($\text{M} = \text{Mn}, \text{Fe}$) the estimated intralayer coupling constant values, J/k_B , were -19.6 and -32.9 K, respectively. This indicates antiferromagnetic coupling between the M^{II} and $[\text{TCNE}]^{\bullet-}$ leading to bulk ferrimagnetic ordering. This agrees with previously reported magnetic data. For $\text{Mn}(\text{TCNE})[\text{C}_4(\text{CN})_8]_{1/2}$, the intralayer coupling was assumed to be the same as compound $[\text{Mn}(\text{TCNE})(\text{NCMe})_2]^+$ since they share similar 2-D layers, and the interlayer coupling constant, K/k_B , was estimated as -1.02 K for **2**. This suggests that the interlayer interaction is antiferromagnetic and leads to bulk antiferromagnetic ordering, as observed. Finally, the coupling constant for 3-D $\text{Mn}(\text{TCNE})_{3/2}(\text{I}_3)_{1/2}$ was shown to be between 1.5 and 2 times as large as that of analogous 2-D analogue $[\text{Mn}(\text{TCNE})(\text{NCMe})_2]^+$. This discrepancy is attributed to the increase of corrugation that is observed in the former with respect to the latter. Therefore, a model that includes the topology is needed to provide a more accurate description for these magnetic materials. As noted, MF theory can overestimate T_c by as much as 40%, but the ratio of interlayer and intralayer coupling (J/K or J/J') should be more quantitatively accurate.

ASSOCIATED CONTENT

Supporting Information

The derivation of the MF expressions for all structure-types. 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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REFERENCES

- Ovcharenko, V. I.; Sagdeev, R. Z. *Russ. Chem. Rev.* **1999**, *68*, 345.
- Blundell, S. J.; Pratt, F. L. *J. Phys.: Condens. Matter* **2004**, *16*, R771.

Table 3. Summary of the Computed Antiferromagnetic Intra- and Interlayer Exchange Couplings

magnet	type	interlayer coupling, K/k_B , or J'/k_B , K	intralayer coupling, J/k_B , K	equation	
2-D Compounds					
$[\text{Mn}(\text{TCNE})(\text{NCMe})_2][\text{SbF}_6]$	1a	A	0^a	-19.6	2, 3
$[\text{Fe}(\text{TCNE})(\text{NCMe})_2][\text{SbF}_6]$	1b	A	0^a	-33.9	2, 3
$[\text{Fe}(\text{TCNE})(\text{NCMe})_2][\text{FeCl}_4]$	1c	A	0^a	-31.8	2, 3
3-D Compounds					
$\text{Mn}(\text{TCNE})[\text{C}_4(\text{CN})_8]_{1/2}$	2	B	-1.02 (K)	-19.6^a	4
			-0.42 (K) ^b		
$\text{Mn}(\text{TCNE})_{3/2}(\text{I}_3)_{1/2}$	3	C_2	-64.2 (J')	-19.6^a	5
$\text{Mn}(\text{TCNE})_{3/2}(\text{I}_3)_{1/2}$	3	C_2	-40.4 ($J' = J$)	-40.4 (J)	2,6
$V(\text{TCNE})_x$		C_2^a		-146 (J)	2,6
		D_2^a		-160 ($J' = J$)	8
				-100 (J) ^c	

^aAssumed. ^bReference 21. ^cBloch law.²⁷

- (3) Miller, J. S. *Chem. Soc. Rev.* **2011**, *40*, 3266. Miller, J. S.; Epstein, A. J. *Angew. Chem. Int. Ed.* **1994**, *33*, 385.
- (4) Miller, J. S. *Angew. Chem. Int. Ed.* **2006**, *45*, 2508.
- (5) Yee, G. T.; Manriquez, J. M.; Dixon, D. A.; McLean, R. S.; Groski, D. M.; Flippen, R. B.; Narayan, K. S.; Epstein, A. J.; Miller, J. S. *Adv. Mater.* **1991**, *3*, 309.
- (6) Miller, J. S.; Calabrese, J. C.; McLean, R. S.; Epstein, A. J. *Adv. Mater.* **1992**, *4*, 498.
- (7) Lapidus, S. H.; McConnell, A. C.; Stephens, P. W.; Miller, J. S. *Chem. Commun.* **2011**, *47*, 7602.
- (8) Stone, K. H.; Stephens, P. W.; McConnell, A. C.; Shurdha, E.; Pokhodnya, K. I.; Miller, J. S. *Adv. Mater.* **2010**, *22*, 2514.
- (9) Manriquez, J. M.; Yee, G. T.; McLean, R. S.; Epstein, A. J.; Miller, J. S. *Science* **1991**, *252*, 1415.
- (10) Miller, J. S. *Polyhedron* **2009**, *28*, 1596.
- (11) Pokhodnya, K. I.; Bonner, M.; Her, J.-H.; Stephens, P. W.; Miller, J. S. *J. Am. Chem. Soc.* **2006**, *126*, 15592.
- (12) Olson, C.; Heth, C. L.; Lapidus, S. H.; Stephens, P. W.; Halder, G. J.; Pokhodnya, K. I. *J. Chem. Phys.* **2011**, *135*, 024503.
- (13) Her, J.-H.; Stephens, P. W.; Ribas-Ariño, J.; Novoa, J. J.; Shum, W. W.; Miller, J. S. *Inorg. Chem.* **2009**, *48*, 3296.
- (14) Miller, J. S.; McLean, R. S.; Vazquez, C.; Calabrese, J. C.; Zuo, F.; Epstein, A. J. *J. Mater. Chem.* **1993**, *3*, 215.
- (15) Her, J.-H.; Stephens, P. W.; Pokhodnya, K. I.; Bonner, M.; Miller, J. S. *Angew. Chem. Int. Ed.* **2007**, *46*, 1521.
- (16) McConnell, A. C.; Shurdha, E.; Miller, J. S. *J. Phys. Chem.* **2012**, *116*, DOI: 10.1021/jp305523t.
- (17) White, R. M. *Quantum Theory of Magnetism*; Springer: Berlin, 2007; pp 149–153. Smart, J. S. *Am. J. Phys.* **1955**, *23*, 356.
- (18) Erickson, R. P.; Mills, D. L. *Phys. Rev. B* **1991**, *43*, 11527.
- (19) (a) Verdaguer, M.; Bleuzen, A.; Marvaud, V.; Vaissermann, J.; Seuleiman, M.; Desplanches, C.; Sculler, A.; Train, C.; Garde, R.; Gelly, G.; Lomenech, C.; Rosenman, I.; Veillet, P.; Cartier, C.; Villain, F. *Coord. Chem. Rev.* **1999**, *190–192*, 1023. (b) Tanaka, H.; Okawa, N.; Kawai, T. *Solid State Commun.* **1999**, *110*, 191. (c) Greedan, J. E.; Chien, C.-L.; Johnston, R. G. *J. Solid State Chem.* **1976**, *19*, 155. (d) Greedan, J. E. *J. Phys. Chem. Solids* **1971**, *32*, 819. (e) Kimishima, Y.; Ichihyanagi, Y.; Shimizu, K.; Mizuno, T. *J. Magn. Magn. Mater.* **2000**, *210*, 244.
- (20) Miller, J. S. *Chem. Soc. Rev.* **2011**, *40*, 3266.
- (21) $|K|$ was calculated by using the relationship $K = -\mu_B H_c (S - S')/S^2$ where $\mu_B = 9.27 \times 10^{-27}$ J/T, $H_c = 1.95$ T, and $S = 5/2$, $S' = 1/2$.
- (22) Drillon, M.; Panissod, P.; Rabu, P.; Souletie, J.; Ksenofontov, V.; Gütlisch, P. *Phys. Rev. B* **2002**, *65*, 104404. Drillon, M.; Panissod, P. *J. Magn. Magn. Mater.* **1998**, *188*, 93. Drillon, M.; Panissod, P. in *Magnetism - Molecules to Materials*; Miller, J. S.; Drillon, M., Eds.; Wiley-VCH: Weinheim, 2003; Vol. 4, p 233.
- (23) Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Chittipeddi, S. R.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769.
- (24) (a) Manson, J. L. In *Magnetism: Molecules to Materials V*; Miller, J. S., Drillon, M.; Eds.; Wiley-VCH: New York, 2001; pp 70–101. (b) Kmety, C. R.; Manson, J. L.; Huang, Q.-Z.; Lynn, J. W.; Erwin, R. W.; Miller, J. S.; Epstein, A. J. *Mol. Cryst. Liq. Cryst. A* **1999**, *334*, 631. (c) Kohout, J.; Jager, L.; Hvastijova, M.; Kozisek, J. *J. Coord. Chem.* **2000**, *51*, 169. (d) Batten, S. R.; Murray, K. S. *Coord. Chem. Rev.* **2003**, *246*, 103.
- (25) Ribas-Ariño, J.; Novoa, J. J.; Miller, J. S. *J. Mater. Chem.* **2006**, *16*, 2600.
- (26) Hibbs, W.; Rittenberg, D. K.; Sugiura, K.-i.; Burkhart, B. M.; Morin, B. G.; Arif, A. M.; Liable-Sands, L.; Rheingold, A. L.; Sundaralingam, M.; Epstein, A. J.; Miller, J. S. *Inorg. Chem.* **2001**, *40*, 1915.
- (27) Pokhodnya, K. I.; Epstein, A. J.; Miller, J. S. *Adv. Mater.* **2000**, *12*, 410. Pokhodnya, K. I.; Pejakovic, D.; Epstein, A. J.; Miller, J. S. *Phys. Rev. B* **2001**, *63*, 174408. Kaneyoshi, T. *Introduction to Amorphous Magnets*; World Scientific: Singapore, 1992; p 92.
- (28) Taliaferro, M. L.; Thorum, M. S.; Miller, J. S. *Angew. Chem. Int. Ed.* **2006**, *45*, 5326.
- (29) Pokhodnya, K. I.; Lefler, B.; Miller, J. S. *Adv. Mater.* **2007**, *19*, 3281.
- (30) Ferlay, S.; Mallah, T.; Ouahes, R.; Veillet, P.; Verdaguer, M. *Nature* **1995**, *378*, 701.
- (31) Verdaguer, M.; Girolami, G. S. In *Magnetism - Molecules to Materials*; Miller, J. S.; Drillon, M., Eds.; Wiley-VCH: Weinheim, 2005; Vol. 5, p 283. Hashimoto, K.; Ohkoshi, S. *Phil. Trans. R. Soc. London A* **1999**, *357*, 2977. Verdaguer, M.; Bleuzen, A.; Marvaud, V.; Vaissermann, J.; Seuleiman, M.; Desplanches, C.; Sculler, A.; Train, C.; Garde, R.; Gelly, G.; Lomenech, C.; Rosenman, I.; Veillet, P.; Cartier, C.; Villain, F. *Coord. Chem. Rev.* **1999**, *190–192*, 1023.
- (32) Holmes, S. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1999**, *121*, 5593.
- (33) Hatlevik, Ø.; Buschmann, W. E.; Zhang, J.; Manson, J. L.; Miller, J. S. *Adv. Mater.* **1999**, *11*, 914.