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Anomalous Stoichiometry, 3-D Bridged Triangular/pentagonal Layered Structured Artificial Antiferromagnet for the Prussian Blue Analog $A_3Mn^{II}_5(CN)_{13}$ (A = NMe₄, NEtMe₃). A Cation Adaptive Structure

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ABSTRACT: The shape of the organic cation dictates both the composition and the extended 3-D structure for hybrid organic/inorganic Prussian blue analogs (PBAs) of $A_aMn^{II}_b(CN)_{a+2b}$ (A = cation) stoichiometry. Alkali PBAs are typically cubic with both MC₆

M'N₆ and octahedral coordination sites, and the alkali cation content depends on the M and M' oxidation The reaction of states. $Mn^{II}(O_2CCH_3)_2$ and A^+CN^- (A = NMe₄, NEtMe₃) forms a hydrated material of $A_3Mn^{II}_5(CN)_{13}$ composition. $A_{3}Mn^{II}_{5}(CN)_{13}$ forms а 3-D extended complex,



structural motif with octahedral and rarely observed square pyramidal and trigonal bipyramidal Mn^{II} sites with a single layer motif of three pentagonal and one triangular fused rings. A complex pattern of Mn^{II}CN chains bridge the layers. (NMe₄)₃Mn^{II}₅(CN)₁₃ possesses one low-spin octahedral and four high-spin pentacoordinate Mn^{II} sites, and orders as an antiferromagnet at 11 K due to the layers being bridged and antiferromagnetically coupled by the non-magnetic cyanides. These are rare examples of intrinsic, chemically prepared and controlled artificial antiferromagnets, and have the

advantage of having controlled uniform spacing between the layers as they are not physically prepared via deposition methods. A₃Mn₅(CN)₁₃ (A = NMe₄, NEtMe₃) along with [NEt₄]₂Mn^{II}₃(CN)₈, [NEt₄]Mn^{II}₃(CN)₇, and Mn(CN)₂ form stoichiometrically related A_aMn^{II}_b(CN)_{a+2b} (a = 0, b = 1; a = 2, b = 3; a = 1, b = 3; and a = 3, b = 5) series possessing an unprecedented stoichiometries and lattice motifs. This These unusual structures and stoichiometries are attributed to the very ionic nature of the high-spin N-bonded Mn^{II} ion that enables the maximization of the attractive van der Waals interactions via minimization of void space via a reduced ∠MnNC. This A_aMn^{II}_b(CN)_{a+2b} family of compounds are referred to as being cation adaptive which size and shape dictates both the stoichiometry and structure.

INTRODUCTION

Several mixed-metal hexacyanometalates possessing the face centered cubic (fcc) (a ~ 10.5 Å) Prussian blue structural motif magnetically order with critical temperatures, T_c , as high as ~100 °C.¹⁻³ The relatively high T_c 's are attributed to the strong superexchange via the conjugated -M'-N=C-M-C=N-M'- linkages.⁴ Albeit structurally related, Prussian blues can have several compositions, e.g. $M'^{III}_4[M^{III}(CN)_6]_3$, $A^+M'^{III}[M^{III}(CN)_6]_3$, $A^+M'^{III}[M^{III}$ $M'^{\parallel}_{3}[M^{\parallel}(CN)_{6}]_{2}$, $A^{+}M'^{\parallel}[M^{\parallel}(CN)_{6}]$, $A^{+}_{2}M'^{\parallel}[M^{\parallel}(CN)_{6}]$, and $M'^{\parallel}[M^{\parallel}(CN)_{6}]$ (A^{+} = alkali cation) that are typically solvated. The canonical unit cell contains significant void space that can accommodate the A⁺ and/or water, and in some cases $[M(CN)_6]^{n-}$ anions are missing. $A_2Mn^{II}[Mn^{II}(CN)_6]$ (A = Na,⁵ K,⁶ Rb⁶), however, has the same framework topology, but a distorted lattice with nonlinear -M'-N=C- linkages with an average \angle M'-N=C << 180°. Use of the larger NEt⁴⁺ forms the layered (2-D) ferrimagnet [NEt₄]₂Mn^{II}₃(CN)₈ and 3-D bridgedlayered antiferromagnet $[NEt_4]Mn^{II}_3(CN)_7$ that can be thermally decomposed to $Mn(CN)_2$ with an interpenetrating diamondoid structure.⁸ To study the effect of cation size in Prussian blue related magnets, and to identify new magnetic materials and structural motifs, we investigated NMe₄⁺ and NEtMe₃⁺ to target A₂Mn^{II}[Mn^{II}(CN)₆] (A = NMe₄, NEtMe₃). [NMe₄]Mn^{II}[Cr^{III}(CN)₆]•4H₂O^{9a} and [NMe₄]Mn^{II}[M^{III}(CN)₆]•8H₂O (M = Mn, Fe)^{9b} have been reported to have non-cubic orthorhombic and tetragonal structures, respectively, but with $\angle M'-N=C = 180^\circ$. Herein, we report the unexpected new structural bridged layered motif of $A_3Mn^{II}_5(CN)_{13}$ (A = NMe₄, NEtMe₃) stoichiometry, and establish

their antiferromagnetic ordering arising from antiferromagnetic coupling between adjacent ferrimagnetic layers. Additionally, an overview of related family members reveals a stoichiometric and structural relationship based on the concept of cation adaptive structures and stoichiometry.

EXPERIMENTAL SECTION

All syntheses were performed in an oxygen-free (<1.0 ppm O₂) wet or dry box. Anhydrous $Mn(O_2CMe)_2$ was used as purchased from Aldrich. 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.

[NMe₄]CN was prepared from [NMe₄][BF₄] (1.30 g, 8.07 mmol) that was added a 10 mL acetonitrile solution containing [NEt₄]CN (1.265 g, 8.10 mmol). After stirring for 24 hr the white solid was then collected and washed with cold acetonitrile (3 x 5 mL) and then placed under vacuum for 5 hr. The white solid is then dissolved in a minimal amount of methanol, filtered, and the methanol is removed under vacuum (Yield: 517 mg, 5.16 mmol, 64%). v_{CN} 2050 cm⁻¹.

[NEtMe₃]CI was made via Schlenk line techniques. To a stirring 13 mL CH₂Cl₂solution of N,N-ethyldimethylamine (1.46 g, 19.9 mmol) in a salt water ice bath was added a 5 mL CH₂Cl₂ solution of methylchloroformate (1.39 g, 14.7 mmol) drop-wise over 10 min. After warming to room temperature for 8 hr a white precipitate formed, and the solution was heated for 1 hr. After cooling the [NEtMe₃]Cl precipitate was isolated via filtration, and washed with 5 x 5 mL of cold dichloromethane before drying under reduced pressure (Yield: 1.3393 g, 74%). IR (KBr): 3374 (br, s), 3009 (m), 1017 (s), 960 (s), 882 (s) cm⁻¹; ¹H NMR (300 MHz, D₂O, 25 °C) δ :1.30-1.365 (tt, *J*₁=7.29 Hz, *J*₂=2.13 Hz, 2H), 3.06 (s, 9H), 3.33-3.40 (q, *J*=7.35 Hz, 3H).

[NEtMe₃]CN was made from a 10 mL methanol solution of [NEtMe₃]Cl (3.49 g, 28.3 mmol) that was added to a stirred 25 mL cloudy methanol solution containing NaCN (2.4 g, 49.2 mmol). A white precipitate formed, and the reaction was stirred for 18 hr. After which the slurry was filtered through Celite[®], and the filtrate was taken to dryness resulting in an off-white/pink solid. To the reaction flask containing the solid was added

40 mL of dry MeCN and stirred for 4 hr, and then again filtered through Celite, and the [NEtMe₃]CN filtrate was taken to dryness to isolate product (Yield: 1.36 g, 42%). IR (KBr) 3426 (br, s), 3007 (m), v_{CN} 2072 (m), 1019 (s), 960 (s), 880 (s) cm⁻¹; ¹H NMR (300 MHz, D₂O, 25 °C) δ :1.29 (tt, *J*₁=7.29 Hz, J₂= 2.01 Hz, 2H), 3.06 (s, 9H), 3.36 (q, 3H).

[NMe4]₃**Mn**₅**(CN)**₁₃•**zH**₂**O (1**•**H**₂**O).** [NMe4]CN (517 mg, 5.16 mmol) was dissolved in a 5 mL of H₂O, and the solution was dropwise added to a 5 mL aqueous solution containing Mn(O₂CMe)₂ (255 mg, 1.47 mmol). A yellow precipitate formed that turned light green, and the mixture was stir for ~12 hr. The light green solid was then filtered, using a medium frit, washed with H₂O (2 x 5 mL), MeOH (2 x 5 mL), and Et₂O (2 x 5 mL). The solid was then placed under vacuum, on the frit, for 2 hr and then isolated (Yield 250 mg; 98%). The solvent content z = 2 was determined from thermogravimetric analyses. The solvent is evident by the v_{OH} at 3658 and 3633 cm⁻¹. Calculated for (NMe4)₃Mn₅(CN)₁₃•3.5H₂O: C₂₅H₄₃Mn₅N₁₆O_{3.5}%(calc'd): C: 33.67 (33.42); H: 4.23 (4.82); N: 24.51 (24.94); Mn: 30.16 (30.57). IR (KBr) v_{CN} ; 2137 (w), 2110 (w), 2073 (s), 2047 (s).

[NMe4]₃Mn₅(CN)₁₃•zMeOH (1•MeOH). [NMe4]CN (510 mg, 5.09 mmol) was dissolved with 5 mL MeOH, and this solution was dropwise added to a vigorously stirred MeOH solution (10 mL) containing Mn(O₂CCH₃)₂ (250 mg, 1.44 mmol). A yellow precipitate formed that turned green. The mixture was stirred overnight (~12 hr). The green solid was filtered using a medium frit and washed with MeOH (2 x 5 mL) and Et₂O (2 x 5mL). The product was dried in vacuo for 2 hr (Yield 245 mg, 97%). The solvent content z = 1.25 (S = MeOH) was determined from thermogravimetric analyses. IR (KBr) ν_{CN} ; 2137 (w), 2110 (w), 2074 (s), 2048 (s). The peaks and positions in the ν_{CN} (2134, 2108, 2075, and 2050 cm⁻¹) region are the same, but with differing in peak intensities.

[NEtMe₃]₃Mn₅(CN)₁₃•H₂O (2•H₂O). Using [NEtMe₃]CN (107.1 mg; 0.938 mmol) and Mn(O₂CCH₃)₂ (54.5 mg, 0.315 mmol) the aforementioned reaction was repeated and the grey precipitate turned yellow within minutes. The reaction mixture was left to stir for 24 hr. The precipitate was isolated via filtration and washed with methanol (4 x 3 mL) and ether (3 x 3 mL), and dried under vacuum at room temperature for 4 hr (Yield: 39.80 mg, 72%). IR (KBr) ν_{OH} 3629 (w, br), ν_{CN} 2141(w), 2098 (m), 2075 (s), 2049 (s), and 1017 (m), 964 (w), 881 (w) cm⁻¹.

Page 5 of 30

Thermogravimetric analysis (TGA) was performed on a TA Instrument Q500 series equipped with an evolved gas furnace and attached to a Pfeiffer Thermostar GSD 301 mass spectrometer. This instrument was located in a Vacuum Atmospheres DriLab box under nitrogen to protect air and moisture sensitive samples. Samples were placed in an aluminum pan and heated at 2 °C/min under a continuous 10-mL/min N₂ flow. Infrared spectra (400 to 4000 cm⁻¹; ±1 cm⁻¹ resolution) were obtained on a Bruker Tensor 37 FT IR spectrophotometer as KBr pellets.

Magnetic susceptibilities were measured in 1000 Oe applied fields between 5 and 300 K on a Quantum Design MPMS 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.¹⁰ Powder samples for magnetic measurements were loaded in gelatin capsules. The temperature dependence of the magnetization was obtained by cooling in zero-field and collecting the data on warming. The remnant magnetization was taken in zero applied field upon warming after cooling in a 5 Oe field. AC susceptibilities were measured at 33, 100, and 1000 Hz. In addition to correcting for the diamagnetic contribution from the sample holder, the Pascal core diamagnetic corrections were used.

Powder X-ray diffraction (PXRD) measurements for Rietveld structure analyses were performed at Beam Line X16C of the National Synchrotron Light Source at Brookhaven National Laboratory. The powdered samples were held in an 1.0-mm diameter thin-wall quartz capillary. Monochromatic X-rays were selected by a Si(111) channel-cut monochromator; diffracted 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.^{11,12} Additional powder X-ray diffraction patterns were collected on all samples with a Bruker D8 Diffractometer (Cu K_{α}) using Mica (NIST Standard Reference Material 675) as an internal standard. Images of structures generated using CrystalMaker[®]; CrystalMaker Software Ltd, Oxford, UK.

RESULTS

The reaction of [NMe₄]CN and Mn(O₂CMe)₂ formed a dark green precipitate as both the hydrate, **1**•H₂**O**, and methanol solvated **1**•MeOH depending on these solvents. Use of [NEtMe₃]CN forms light-green **2**•H₂**O** using aqueous media.¹³ The compositions of **1**•H₂**O**, **1**•MeOH, and **2**•H₂**O** were unknown prior to structure determination by real space simulated annealing, model building, and Rietveld refinement from the powder samples (Figure 1). The powder diffraction patterns of **1**•H₂**O** and **1**•MeOH are sufficiently similar to conclude that they are isostructural, but the former is much better resolved; thus, the analysis is restricted to the hydrate. At ambient temperature, **1**•H₂**O** has hexagonal lattice parameters *a* = 13.6227(4) Å, *c* = 5.7794(2) Å (extinction symbol *P*---, eventually determined space group $P\overline{6}2m$, *Z* = 1) and **2**•H₂**O** has *a* = 13.5280(6) Å, *c* = 17.8231(8) Å (extinction symbol *P*₃₁--, space group *P*₃₁21, *Z* = 3). By inspection of the powder diffraction patterns, they do not have the face centered cubic (*fcc*) structure that is typical of Prussian blue compounds, or any simple distortion thereof.^{14,15} The Rietveld refinements yield water contents *z* ~ 2.0(1) for **1**•H₂**O** and *z* ~ 0.33(5) for **2**•H₂**O**, consistent with the elemental and thermogravimetric analyses.



Figure 1. High-resolution synchrotron powder diffraction data (dots) and Rietveld fit of the data for $1 \cdot H_2O$ (top) and $2 \cdot H_2O$ (bottom). The lower trace is the differences, measured – calculated, plotted to the same vertical scale.

Structure

The close similarity of their *a* lattice parameters, and that the *c* lattice parameters of $1 \cdot H_2O$ and $2 \cdot H_2O$ are close to a ratio of 1:3, and overall similarity of their diffraction patterns imply that $1 \cdot H_2O$ and $2 \cdot H_2O$ have very similar structures, which is borne out in the eventual structural analysis. $1 \cdot H_2O$ turns out to be a more disordered version of $2 \cdot H_2O$, and to clarify that the disorder is intrinsic, data on the same sample of $1 \cdot H_2O$ was also collected at 22 K. It is more straightforward and convincing to describe disordered $1 \cdot H_2O$ in the context of ordered $2 \cdot H_2O$; for that reason, the ordered structure of $2 \cdot H_2O$ is initially described. Crystallographic details are given in Table 1.

	1•H₂O (1• 2H ₂ O)	1•H₂O (1• 2H ₂ O)	2•H₂O (2• 0.33H ₂ O)
Formula	(N(CH ₃) ₄) ₃ Mn ₅ (CN) ₁₃ (N(CH ₃) ₄) ₃ Mn ₅ (CN) ₁₃		(N(C ₂ H ₅)(CH ₃) ₃) ₃ Mn ₅ (CN) ₁₃
	•2H ₂ O	•2H ₂ O	•0.33H ₂ O
	$C_{25}H_{40}N_{16}Mn_5O_2$	$C_{25}H_{40}N_{16}Mn_5O_2$	C ₂₉ H _{42.67} N ₁₆ Mn ₅ O _{0.33}
Formula mass	869.35	869.35	882.79
<i>T</i> , K	295	22	295
Space Group	P 6 2 <i>m</i> (#189)	P 6 2 <i>m</i> (#189)	<i>P</i> 3 ₁ 21 (#152)
<i>a</i> , Å	13.6227(4)	13.5940(12)	13.5280(6)
<i>c</i> , Å	5.7794(2)	5.7260(6)	17.8231(8)
Ζ	1	1	3
V, Å ³	928.82	916.4(2)	2824.77
$ ho_{ ext{calcd}}$, g/cm 3	1.55	1.57	1.56
R _{wp} a	5.89 %	6.63 %	4.94 %
R _{exp} b	3.88 %	3.11 %	1.68 %
R _{Bragg}	2.28 %	2.54 %	2.53 %
Pawley R _{wp}	4.95 %	5.77 %	3.13 %
<i>λ</i> , Å	0.69977(2)	0.69997(6)	0.69983(3)

Table 1. Summary of crystallographic results for **1**•H₂O and **2**•H₂O.

a $R_{wp} = \sqrt{\frac{\sum_{i}^{i} w_i (y_i^{calc} - y_i^{obs})^2}{\sum_{i}^{i} w_i (y_i^{obs})^2}}$, where y_i^{calc} and y_i^{obs} are the calculated and observed intensities

at the *i*th point in the profile, including background, normalized to monitor intensity. The weight w_i is $1/\sigma^2$ from counting statistics, with the same normalization factor.

$$R_{\rm p} = \sqrt{\frac{\sum_{i} (y_i^{calc} - y_i^{obs})^2}{\sum_{i} (y_i^{obs})^2}}$$

Page 9 of 30

The *a-b* planes of **2·H₂O** has a network of Mn^{II} connected by CN groups, forming three- and five-membered rings, Figure 2a. Each layer of **2·H₂O** has three chemically distinct Mn^{II} ions (Figure 2b). Mn1 is a 5-coordinate square pyramid with two locations in each plane; Mn2 is a 5-coordinate trigonal bipyramid with two locations in each plane, and Mn3 is octahedrally coordinated, with one location in each plane. It should be noted both 5-coordinate square pyramidal and trigonal bipyramidal Mn^{II} sites are unusual, with Mn(NO)(CO)₄ being a rare example,¹⁶ although these geometries are observed for $[Cr^{II}(CN)_5]^{3-.17}$

Perpendicular to the plane, Mn1 and Mn3 form Mn1-N-C-Mn3-C-N-Mn1 chains, Figure 3a, with the 5.25 Å Mn1-Mn3 distance being typical of Prussian blue structured compounds. The triangular Mn1-N-C-Mn3-C-N-Mn1 component possesses each of the three Mn's noted in Figure 3a such that a layer is connected to the layer above and below it, Figure 3b (and movie S1).

The Mn2 sites, illustrated in Figure 3c, are separated by 5.94 Å, which is unprecedentedly long for an Mn-C-N-Mn linkage as they typically are ~5.25 Å.^{1,15} The refinement presented here has a disordered CN between two Mn2 sites along the *c* axis, but the distances are unusual: Mn2-(C/N) = 2.34 Å, and C-N = 1.27 Å. Models with split sites for Mn2 or the bridging CN give marginally better R-factors, but none of them is sufficiently compelling, either from a chemical standpoint or from improvement of the structural refinement, to be regarded as a definitive structure. The NEtMe₃⁺ cations reside in two distinct sites located within the cavities between the layers in the five-membered rings. A small amount of solvent water appears in the void between adjacent Mn1 sites.



Figure 2. Structure a single layer of the $2 \cdot H_2 O$ looking normal to the *ab* plane (top), and the complete unit cell viewed along the *c* axis (bottom) (C is black, N is light blue, and orientationally disordered C/N is dark blue, Mn is magenta (H atoms are not shown).



Figure 3. a) Structure of the Mn1-NC-Mn3-CN-Mn1 in **2**•H₂**O**, showing coordination by five, six, and five cyanides, respectively (N light blue, C black, disordered N/C dark blue). b) Triangular column illustrating that every layer (gray) has two square pyramidal Mn1 sites connected to an octahedral Mn3 site in a different layer. The blue, brown and red coloring illustrates the registration of the Mn1-NC-Mn3-CN-Mn1 sequences between layers. Movie S1 depicts this unusual arrangement more clearly. c) Structure of infinite -Mn2-(C/N)-Mn2- chains in **2**•H₂**O**.

The results of X-ray diffraction do not convincingly distinguish the C from the N atoms on the basis of scattering amplitude, but the bond distances to the Mn^{II} sites generally clarify the assignments of CN orientations. Some of the cyanides are disordered because they consist of two atoms equivalent by symmetry. Further disorder of the cyanide orientations, not required by symmetry, cannot be excluded; the simplest model consistent with the powder diffraction data is described. The octahedral Mn3 site is coordinated by six C-bound cyanides, Figure 3a, consistent with the propensity of cyanide to bond to an octahedral M site via carbon,^{1,15} The equatorial Mn3-C distances are 1.91(1) and 2.11(1) Å, while the axial Mn3-C distance is 1.91(1) Å. This is not a Jahn-Teller distortion (as observed for Na₄[Mn(CN)₆]•10H₂O,^{18a,b} and K₂Mn[Mn(CN)₆]⁶) because the two long distances are adjacent, not *trans*. The square-pyramidal Mn1 site is N-bonded to three equatorial CN (Mn1-N = 2.11(1) Å, 2.26(1) Å, and 2.26(1) Å) and one symmetry-disordered C/N at 2.38(1) Å [as occurs for Mn^{II}(CN)₂],⁸ and N-bonded (Mn1-N = 2.17 Å) in the axial direction. Due to reduced crystal field stabilization energies, the 5-coordinated Mn1 and Mn2 are assumed to be high spin, as occurs for [Cr^{II}(CN)₅]³⁻ .17

1•H₂**O**, with the slightly smaller NMe₄⁺ cation, has essentially the same in-plane structure as **2•H**₂**O** (Figure 4a), but the Mn1 and Mn3 sites of **2•H**₂**O** become equivalent. Various models of disorder were explored and the Mn1 site, which has 4-fold equatorial coordination in the *ab* plane is significantly extended along the *c* axis, while the Mn2 site (3-fold equatorial coordination) is not. The straightforward interpretation is that **1•H**₂**O** contains the same Mn-cyanide trimers, two square-pyramidal sites joined in the axial direction to an octahedral site, as seen in **2•H**₂**O**, but they are disordered along the *c* axis relative to one another. Alternatively, it may be that the square-pyramidal and octahedral Mn sites are randomly distributed along the channels in a ratio of 2:1. Either model is consistent with the diffraction data and with the necessity to balance charge as [NMe4]₃Mn^{II}₅(CN)₁₃. The model used for refinement, shown in Figure 4b, has three sites for Mn1, each with occupancy of 1/3. Likewise, the refinement favors a split site for the disordered CN that spans the in-plane Mn1-Mn1 connection. The axial Mn1-Mn1 linkages along the *c* axis are 2/3 occupied by a disordered CN, and 1/3 occupied by solvent water.

There is also solvent water between the three-membered rings. The infinite -Mn2-(CN)-Mn2- chains in **1**•H₂**O** are essentially identical to those in **2**•H₂**O**, except that all of the Mn2 sites, with trigonal bipyramidal coordination, appear to be C-bonded to all three of their equatorial cyanides (Figure 4c).





Figure 4. a) View of $1 \cdot H_2O$ along the *c* axis. b) Average configuration of the disordered chains of Mn1-(CN)-Mn1-(NC)-Mn1 in $1 \cdot H_2O$. One third of the axial (C/N) disordered sites are occupied by solvent water (red). c) Structure of infinite -Mn2-(CN)-Mn2- chains in $1 \cdot H_2O$. The color scheme is the same as Figures 2 and 3, plus red for oxygen in solvent water.

The interlayer Mn••••Mn separation, *c*, is 5.78 Å for $1 \cdot H_2O$ and 5.94 for $2 \cdot H_2O$, and are >0.4 Å longer than reported for Cs₂Mn[Mn(CN)₆] (5.303 Å),⁶ [NEt₄]₂Mn^{II}₃(CN)₈ (5.162 Å), and [NEt₄]Mn^{II}₃(CN)₇ (5.115 Å).⁷ This is attributed to the long axial Mn-(C/N) bond in the trigonal bipyramidal sites in both materials, and/or the stacking of the square pyramidal sites, whether ordered in $2 \cdot H_2O$ (Figure 3a), or disordered in $1 \cdot H_2O$ (Figure 4b). The overall 3-D topology is complicated and cannot be reduced to any simple 2-nodal topology.

Magnetic properties

The magnetic susceptibility, χ , of [NMe₄]₃Mn₅(CN)₁₃•S [S = H₂O (**1**•H₂O), MeOH (**1**•MeOH)] and [NEtMe₃]₃Mn₅(CN)₁₃•H₂O (**2**•H₂O) were measured from 5 to 300 K, and are plotted as $\chi(T)$ (Figure 5), $\chi T(T)$, and $\chi^{-1}(T)$ (Figure 6). The $\chi(T)$ for **1**•H₂O, **1**•MeOH, and **2**•H₂O increase with decreasing temperature until they reach sharp maxima at 12.6, 10.1, and 17.1 K, respectively, before decreasing upon further cooling. The cusp-like peaks in $\chi(T)$ are suggestive of antiferromagnetic ordering. $\chi^{-1}(T)$ is linear above 60 K with fitting the data to the Curie-Weiss expression, $\chi \propto (T - \theta)^{-1}$, yields a Weiss constant,

 $\theta \sim -35$ K for **1**•H₂O and **1**•MeOH, and -40.5 K for **2**•H₂O. The significant negative θ -values are further evidence for antiferromagnetic coupling. **1**•H₂O and **1**•MeOH have room temperature χT -values of 16.18 ± 0.01 emuK/mol. **2**•H₂O, however, has a 10% larger room temperature χT -value of 17.55 emuK/mol.¹⁹ Upon cooling $\chi T(T)$ decreases with increasingly greater rates at lower temperatures for each compound.



Figure 5. $\chi(T)$ for $[NMe_4]_3Mn_5(CN)_{13}$ •S (S = H₂O (\blacktriangle), MeOH) (\checkmark), and $[NEtMe_3]_3Mn_5(CN)_{13}$ •H₂O (•) in a 1000 Oe applied field.



Figure 6. a) $\chi T(T)$ and b) $\chi^{1}(T)$ for [NMe₄]₃Mn₅(CN)₁₃•S (S = H₂O (\blacktriangle), MeOH) (\checkmark) and [NEtMe₃]₃Mn₅(CN)₁₃•H₂O (•) in a 1000 Oe applied field. Inset in (a) is $d(\chi T)/dT$ for [NMe₄]₃Mn₅(CN)₁₃•S (S = H₂O (\bigstar), MeOH) (\checkmark), and [NEtMe₃]₃Mn₅(CN)₁₃•H₂O (•). The solid lines are fits to the Curie-Weiss expression (see the text).

These room temperature χT -values for **1·H**₂**O** and **1·MeOH** are substantially lower than the spin-only, *i.e.* $\chi \propto T^{-1}$, expectation of *i*) 21.875 emuK/mol for five high-spin (*hs*) Mn^{II} sites, and *ii*) 17.875 emuK/mol for one low-spin (*ls*) and four *hs* Mn^{II} sites, due to the aforementioned antiferromagnetic coupling. However, above ~25 K $\chi T(T)$ is well fit by the Curie-Weiss expression, $\chi \propto (T - \theta)^{-1}$, with $\theta = -35$ K for **1·H**₂**O** and **1·MeOH** based on one *ls* and four *hs* Mn^{II} sites, Figure 5. The fit is much poorer when all five Mn^{II} sites are assumed to be *hs* or more than one site is *ls*. Higher values of $\chi T(T)$ were obtained for **2·H**₂**O**, Figure 6 top, which cannot be fit to one *ls* and four *hs* Mn^{II} sites.²⁰ A good fit was obtained for 0.5 *ls* and 4.5 *hs* Mn^{II} sites, Figure 6 top. The fractional number of high- and low-spin sites are attributed to all five coordinate sites being *hs*,¹⁷ and the octahedral sites being a mix of *hs* and *ls*, as they will be low spin when all cyanides are C-bonded, but with several N-bonded cyanides, the site should be high spin. This suggests that more of the cyanides are disordered than the simple structural model described above, and and this disorder is more prevalent for **2·H**₂**O** may be a factor in this disorder.

The cusp in the $\chi(T)$ data is additional evidence for antiferromagnetic ordering.²¹⁻ ²⁴ The temperature at which the maximum in $\chi(T)$ occurs lies above T_c ,^{25,26} and T_c can be determined from the temperature at which the maximum in $d(\chi T)/dT$ occurs, *i.e.*, Fisher's specific heat.^{27,28} The $d(\chi T)/dT$ data for **1**•H₂**O**, **1**•MeOH, and **2**•H₂**O** have peaks at 11, 8.8, and 14 K, respectively, Figure 6 top inset, which are their antiferromagnetic ordering temperatures, T_c , respectively. The higher T_c for **2**•H₂**O** is in accord with 10% more high spin S = 5/2 Mn(II), and less low spin S = 1/2 Mn(II) being present with respect to **1**•H₂**O**, as $T_c \propto S(S + 1)$.^{1,29,30}

The field dependent magnetization, M(H), at 5 K from ±90 kOe is linear and is still increasing with applied field, and is 27,000, 28,750, 38,700 emuOe/mol at 90 kOe for **1**•H₂O, **1**•MeOH, and **2**•H₂O respectively, with no evidence of a saturation or a remnant magnetization, or a coercive field, Figure 7, as is expected for an antiferromagnet.



Figure 7. 5 K M(H) for $[NMe_4]_3Mn_5(CN)_{13}$ •S (S = H₂O (\blacktriangle), MeOH (\checkmark)), and $[NEtMe_3]_3Mn_5(CN)_{13}$ •H₂O (•).

The in-phase, real, $\chi'(T)$, and out-of-phase, complex, $\chi''(T)$, components of the AC susceptibility for **1**•H₂**O**, **1**•MeOH, and **2**•H₂**O** are also characteristic of antiferromagnetic ordering, Figure 8, as $\chi''(T)$ is not evident. The $\chi'(T)$ data are frequency independent. The maximum in the 33-Hz $\chi'(T)$ data occur at 13.5, 10.4, and 19 K for **1**•H₂**O**, **1**•MeOH, and **2**•H₂**O**, respectively, and are a little higher, but in accord with T_c . The broader peak for **2**•H₂**O** is attributed to Et group disorder present in the lower symmetry cation with respect to NMe₄⁺.



Figure 8. Real, $\chi'(T)$ (filled symbols), and imaginary, $\chi''(T)$ (hollow symbols), AC susceptibilities for [NMe4]₃Mn₅(CN)₁₃•S [S = H₂O, MeOH)] and [NEtMe₃]₃Mn₅(CN)₁₃•H₂O (green) at 33 (red), and 100 (green), and 1000 (blue) Hz.

The small magnetic irreversibility observed in the $\chi''(T)$ data is not intrinsic. It is attributed to the unusual nature of this antiferromagnet arising from antiferromagnetic coupling of ferromagnetically ordered layers, and not opposing equivalent paramagnetic spins, and is presumably due to defects sites or impurities that results in incomplete compensation via antiferromagnetic coupling. Similarly, a small magnetic irreversibility is observed in the M(T) data, and while unexpected for antiferromagnetic ordering materials, it has been reported.^{27,31} Furthermore, this behavior has also been observed for [NEt₄]Mn^{II}₃(CN)₇⁷ and M(TCNE)[C₄(CN)₈]_{1/2} (M = Mn, Fe)³² antiferromagnets, but is not observed for antiferromagnets arising from antiferromagnetic coupling of the identical spin site, *e.g.* Mn(CN)₂,^{8]} or the more classical antiferromagnets.

Triangular and pentagonal arrangements of magnetic spin sites, as occurs for **1·H₂O**, **1·MeOH**, and **2·H₂O** should lead to magnetically frustrated materials.^{33,34} Magnetic frustration can be assessed from the figure-of-merit, $f \{= |\theta|/T_c\}$.³³ For f < 5 frustration is minimal, but for f > 10 it is significant, as occurs for many compounds.^{26,33-35} The *f* values are <3.6 for these compounds (Table 2), and indicate that **1·H₂O**, **1·MeOH**, and **2·H₂O** are only minimally magnetically frustrated. As every triangle and pentagon contains only one low-spin Mn^{II} site, the frustration should not be as pronounced as it would be if all spins were identically high spin. Furthermore, significant, non-frustrated antiferromagnetic coupling occurs between these layers via cyanide bridges.–Spin glass behavior can contribute magnetic frustration, but, as $\chi'(T)$ is frequency independent, this can be ruled out.³⁶

A	[NMe ₄] ⁺	[NMe ₄] ⁺	[NEtMe ₃] ⁺
•S	•2H ₂ O	•1.25MeOH	•0.41H ₂ O
$\chi_{\rm obs} T$, emuK/mol (300 K)	16.17ª	16.19 ^a	17.55 ^a
_{Xcalc} T, emuK/mol (spin-only): 5Mn ^{II} hs	21.875	21.875	21.875
_{Xcalc} T, emuK/mol (spin-only): 4Mn ^{ll} hs+Mn ^{ll} ls	17.875	17.875	17.875
$\chi_{calc} T$, emuK/mol (CW; Φ): 5Mn ^{II} hs	19.59	19.59	19.27
$\chi_{calc}T$, emuK/mol (CW; ϕ): 4Mn ^{II} hs +Mn ^{II} ls	16.01	16.01	15.75
χ_{calc} T, emuK/mol (CW; ϕ): 4.5Mn ^{II} hs +0.5Mn ^{II} ls	16.86	16.86	17.13
θ, ^b K (Curie-Weiss)	-35	-35	-40.5
T_{cusp} [Cusp or maximum in $\chi(T)$]	12.6	10.1	17.1
$T_{\rm c} [T_{\rm max} \text{ for } d(\chi T)/dT]$	11	8.8	14
$T_{\rm c}$, K (AC) from $\chi'(T)$ (33 Hz)	13.5	10.4	19
$f = \theta /T_{\rm c}^{33}$	3.6	3.4	2.9
<i>M</i> , emuOe/mol (5 K, 90 kOe), emuOe/mol	27,000ª	28,750ª	38,700ª

Table 2. Summary of Magnetic Properties for 1•H₂O, 1•MeOH, and 2•H₂O.

^a Still increasing and not saturated. ^b $\chi \propto (T - \theta)^{-1}$

Discussion

The antiferromagnetic ground states arise from antiferromagnetic coupling via the layer of nonmagnetic cyanides that bridge between adjacent ferrimagnetic layers. Each layer is ferrimagnetic due to the antiferromagnetic coupling between adjacent high- (S = 5/2) and low-spin (S = 1/2) Mn^{II} sites, as occurs for antiferromagnet [NEt₄]Mn^{II}₃(CN)₇ and ferrimagnet [NEt₄]₂Mn^{II}₃(CN)₈.⁷ Hence, A₃Mn₅(CN)₁₃ (A = NMe₄, NEtMe₃) are rare examples of intrinsic artificial antiferromagnets (AAF),³⁷ which are increasingly important for the development of spin valves (albeit using extrinsic, deposition-prepared AAFs).³⁸ These materials along with M(TCNE)[C₄(CN)₈]_{1/2} (M = Mn, Fe³² are the first intrinsic, chemically prepared and controlled AAFs, and have the advantage of having controlled uniform spacing between the layers as they are not physically prepared via deposition methods.

When the unusual structure of $A_3Mn_5(CN)_{13}$ (A = NMe₄, NEtMe₃) is considered along with layered [NEt₄]₂Mn^{II}₃(CN)₈, bridged-layered [NEt₄]Mn^{II}₃(CN)₇,⁶ and interpenetrating diamondoid Mn(CN)₂,⁷ they can be grouped as a stoichiometrically related $A_aMn^{II}_b(CN)_{a+2b}$ (a = 0, b = 1; a = 2, b = 3; a = 1, b = 3; and the present a = 3, b = 5) family each possessing an unprecedented stoichiometry and lattice motif. The extended structure forms around the cation, and its shape and charge lead to unusual stoichiometries and lattices. The driving force is ascribed to the very ionic nature of the high-spin Mn^{II} ion that enables a reduced ∠MnNC to minimize the void space in the lattice. Hence, this $A_aMn^{II}_b(CN)_{a+2b}$ family of compounds are referred to as being cation adaptive which size and shape dictates both the stoichiometry and structure.

Related aspects of the differing compositions and structures have been observed for some oxides as infinitely adaptive structures,³⁹ in addition to dimensional reduction.⁴⁰ Oxides examples include: Ti_xO_{2x-1} (x ≤ 37) [= TiO_n (2 $\geq n \geq 1.75$)], and $M_{2x}O_{(16x-2)/3}$ (M = Mo, Ta) [= y M₁₀O₂₆ + z M₂₂O₅₈]. This is attributed to different and shifting crystallographic shear planes, or ordered stacking for the latter family.

Alternatively, the structures of [NMe₄]₃Mn₅(CN)₁₃ and [NEtMe₃]₃Mn₅(CN)₁₃ may be viewed as "dimensional reduction" albeit with an increase in connectivity that is well known for monoatomic anionic oxides/sulfides and halides.⁴⁰ Hence, it is extended to more complex anions as well as polyatomic cations. Zero dimensional (no extended

structure) is observed for both $[Mn^{II}(CN)_6]^{4-}$ and $[Mn^{II}(CN)_4]^{2-}$ with Mn:CN ratios of 1:6 and 1:4, respectively, while 2-D $[NEt_4]_2Mn^{II}_3(CN)_8$ has Mn:CN of 1:2.67, and 3-D K₂Mn^{II}[Mn^{II}(CN)_6], $[NEt_4]Mn^{II}_3(CN)_7$, and $[NMe_4]_3Mn^{II}_5(CN)_{13}$ have Mn:CN of 1:3.0, 1:2.33, and 1:2.60, respectively. Such complex, but variable stoichiometries are observed for several transition metal oxides.⁴⁰

CONCLUSIONS

The structure of $A_3Mn^{II}{}_5(CN)_{13}$ (A = NMe₄, NEtMe₃) has a complex (and in the case of NMe₄⁺ a very disordered) structure with octahedral, and rare square pyramidal, and trigonal bipyramidal Mn^{II} sites. It has a layer motif based on three pentagons and one triangle perpendicularly interconnected by orientationally disordered cyanides. $A_3Mn^{II}_5(CN)_{13}$ is key member of $A_aMn^{II}_b(CN)_{a+2b}$ (a = 0, b = 1; a = 1, b = 3; a = 2, b = 3; and a = 3, b = 5) that form cation adaptive structures. These unusual stoichiometries and extended lattices are attributed to the highly ionic nature of the high-spin N-bonded Mn^{II} ion that enables the maximization of the attractive van der Waals interactions via a reduced $\angle MnNC$. $A_3Mn^{II}_5(CN)_{13}$ magnetically order as antiferromagnets, and are minimally magnetically frustrated. The intrinsic antiferromagnetic ordering arises from the non-magnetic cyanide layer providing antiferromagnetic coupling between the ferrimagnetic layers that result, as occurs for artificial antiferromagnets used in spin valves.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.XXXXXX.

The powder X-ray crystallographic CIF files for $1 \cdot H_2 O$ (295 and 22 K) and $2 \cdot H_2 O$ (CCDC1543750 -1543752).

A movie showing the interlayer connectivity.

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DEDICATION

Dedicated to the late Hugo Rietveld, on the fiftieth anniversary of the invention of the technique that bears his name, which has revolutionized the applicability of powder diffraction to crystallography

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Notes

The authors declare no competing financial interest.

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Anomalous Stoichiometry, 3-D Bridged Triangular/pentagonal Layered Structured Artificial Antiferromagnet for the Prussian Blue Analog $A_3Mn^{II}_5(CN)_{13}$ (A = NMe₄, NEtMe₃). A Cation Adaptive Structure

Saul H. Lapidus, Peter W. Stephens, Christopher M. Kareis, Casey G. Hawkins, and Joel S. Miller

Atypical of Prussian blue structured materials, Mn^{II} and A(CN) (A = NMe₄, NEtMe₃) react to form $A_3Mn_5(CN)_{13}$ possessing layers of triangles and pentagons. These layers are bridged together in a complex manner, and form non-frustrated artificial antiferromagnets. Unusual square-pyramid and trigonal bipyramid coordination of Mn^{II} cyano coordination is observed in these materials.

