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Article

TCNE Dimer Dianion Coordination Complexes, $[Mn(TPA)(TCNE)]_2[\mu_2\text{-}(TCNE)_2]$ and $[Mn(TPA)(\mu_4\text{-}C_4(CN)_8)_{0.5}]\cdot ClO_4$, TPA = tris(2-Pyridylmethyl)amine: Synthesis, Structure and Magnetic Properties

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The structures and magnetic properties of two products that result from the reactions of $[Mn(TPA)(CH_3CN)_2](ClO_4)_2$, TPA = tris(2-pyridylmethyl)amine and potassium tetracyanoethylenide, KTCNE, are reported. $[Mn(TPA)(TCNE)]_2[\mu_2\text{-}(TCNE)_2]$ (**1**) and $[Mn(TPA)(\mu_4\text{-}C_4(CN)_8)_{0.5}]\cdot ClO_4$ (**2**) are obtained by using two different ratios of the initial reactants. Each was intended to possess two or more *cis*-TCNE radical anions ($TCNE^{\bullet/-}$) as ligands. **1** is a dinuclear species that crystallizes in the triclinic system in the space group $P\bar{1}$, with $a = 10.4432(17)$, $b = 12.2726(16)$, and $c = 13.708(2)$ Å; $\alpha = 88.505(12)$, $\beta = 75.560(14)$, and $\gamma = 87.077(12)°$; $V = 1698.9(4)$ Å^3; and $Z = 1$ and features two metal centers each with three nearly orthogonal $TCNE^{\bullet/-}$ ligands. However, the three $TCNE^{\bullet/-}$ ligands are all dimerized via the formation of four-center, two-electron bonds: two bridge the two Mn(II) centers, and a third $TCNE^{\bullet/-}$ ligand forms an intermolecular bond to another equivalent $TCNE^{\bullet/-}$. **2** crystallizes in the tetragonal system in the space group $P4_22_12$, with $a = 17.170(3)$, $b = 17.170(3)$, and $c = 17.1837(6)$ Å; $V = 5065.9(13)$ Å^3; and $Z = 8$. It consists of a ribbon-like coordination polymer containing the previously observed but still relatively rare octacyanobutyl dianion. The $[C_4(CN)_8]^{2-}$ anion is derived from the dimerization of two TCNE radical anions via the formation of a new σ bond, and each anion bridges four Mn(II) centers. Both **1** and **2** display magnetic behavior consistent with only weak antiferromagnetic coupling between the high-spin d^5 Mn(II) in which the $TCNE^{\bullet/-}$ are rendered diamagnetic through dimerization.

Introduction

We have recently been exploring synthetic routes to discrete multimetallic complexes containing organic radical−anion bridges between spin-containing metal ions for the purposes of modeling the presumed structure of the magnetic phase of $V[TCNE]_2$.[1] This compound is a room-temperature magnet that is structurally amorphous and is hypothesized to be a network of V(II) ions multiply bridged by TCNE radical anions ($TCNE^{\bullet/-}$). The direct evidence for this is scant, however, so our response has been to attempt to synthesize discrete complexes containing the essential elements of this structure, particularly a bridging $TCNE^{\bullet/-}$. This approach has led previously to the isolation of two manganese coordination complexes with two *cis*-$TCNE^{\bullet/-}$ ligands on a metal center, one with terminal $TCNE^{\bullet/-}$ ligands and one with doubly bridging $TCNE^{\bullet/-}$ ligands.[2] In each case, however, the TCNE radicals are stacked to give a diamagnetic dimer dianion, resulting from the formation of a four-center, two-electron π-type bond, not the desired paramagnetic $TCNE^{\bullet/-}$. Thus, the ligands are only radical anions in a formal sense (from an electron-counting perspective) because the radical character is lost upon the formation of new bonds.

Here, we report two new examples of manganese(II) complexes formed from the reaction of a manganese precursor with $TCNE^{\bullet/-}$ that also possess dimer dianions of the TCNE radical: $[Mn(TPA)(TCNE)]_2[\mu_2\text{-}(TCNE)_2]$ (**1**) and $[Mn(TPA)(\mu_4\text{-}C_4(CN)_8)_{0.5}]\cdot ClO_4$ (**2**). To the best of our

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knowledge, **1** is the first example of three TCNE ligands coordinated to one metal center. This compound exhibits both the previously observed intramolecular π-type dimerization of TCNE radicals and an essentially equivalent intermolecular π-type dimerization. **2** is a rare example of a structurally characterized σ-type dimer of TCNE$^{\bullet/-}$, octacyanobutyl dianion,[3] which we distinguish from the π-dimer by writing it as $C_4(CN)_8{}^{2-}$. In the crystal structure, this species bridges four metal centers. Single-crystal X-ray structures and magnetic properties are discussed in terms of the ultimate fate of the TCNE radical anions in these compounds and the relevance of these results to the proposed structure of the V[TCNE]$_2$ magnet.

Experimental Section

General Considerations. All of the syntheses of air-sensitive compounds were carried out in a nitrogen-filled Vacuum Atmospheres glove box and by utilizing standard Schlenk techniques. Reagents were used as received except as noted below. Solvents were distilled from the appropriate drying agent under nitrogen. Dichloromethane and acetonitrile were distilled from P_2O_5. Diethylether was distilled from Na/benzophenone. All of the solvents were degassed with glove box N_2 prior to use.

Synthesis. The ligand TPA, tris(2-pyridylmethyl)amine, and $[Mn(TPA)(CH_3CN)_2](ClO_4)_2$ were prepared according to literature procedures.[4−6] KTCNE was prepared by adding potassium iodide (677 mg, 4.08 mmol) to a solution of TCNE (384 mg, 3.00 mmol) in 10 mL of acetonitrile at room temperature with stirring. The KI dissolved, and 150 mg of KTCNE crystallized from the dark-yellow solution.

Preparation of [Mn(TPA)(TCNE)]$_2$[μ_2-(TCNE)$_2$], 1. To a solution containing $Mn(TPA)(CH_3CN)_2(ClO_4)_2$ (60.0 mg, 0.0958 mmol) in 10 mL of CH_2Cl_2 was added a solution of KTCNE (32.0 mg, 0.192 mmol) in 3 mL of CH_3CN. The mixture was stirred for 30 min at room temperature and then filtered to remove the $KClO_4$. Ether (15 mL) was added slowly to the yellow-brown filtrate to precipitate an air-sensitive brown solid. The solid was filtered, washed with ether, and dried in a vacuum. Recrystallization from CH_3CN afforded black crystals. Yield: 65 mg (56%). IR: ν(CN), 2198, 2180, 2161, and 2143 cm^{-1}. Anal. Calcd for $C_{60}H_{36}Mn_2N_{24}$: C, 59.61; H, 3.00; N, 27.81. Found: C, 59.52; H, 2.97; N, 27.49.

Preparation of [Mn(TPA)(μ_4-$C_4(CN)_8)_{0.5}$]·ClO_4, 2. To a solution of $Mn(TPA)(CH_3CN)_2(ClO_4)_2$ (60.0 mg, 0.0958 mmol) in 10 mL of CH_2Cl_2 was added a solution of KTCNE (16.0 mg, 0.0958 mmol) in 4 mL of CH_3CN. The mixture was stirred for 30 min at room temperature and then filtered to remove the $KClO_4$. Brown crystals were obtained by allowing ether to diffuse into the solution at room temperature. Yield: 16 mg (29%). IR: ν(CN), 2219, 2194, and 2151 cm^{-1}. Anal. Calcd for $C_{24}H_{18}MnN_8ClO_4$: C, 50.32; H, 3.17; N, 19.56. Found: C, 50.82; H, 3.40; N, 18.45.

Hazard Warning. Perchlorate salts are potentially explosive and should be used in small amounts and handled with care.[7]

Physical Measurements. All of the magnetic measurements were performed on a 7 T Quantum Design MPMS SQUID magnetometer. Measurements of magnetization as a function of temperature were performed from 1.8 to 300 K in a 5000 G applied field as indicated. Randomly oriented polycrystalline samples were cooled in a zero applied field and measured upon warming. Samples were prepared as previously described.[8] Diamagnetic corrections were applied based on Pascal's constants for $\chi T(T)$ plots. IR spectra were measured using a MIDAC M-series FTIR. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

X-ray Crystallography. Single crystals of **1** and **2** were prepared by vapor diffusion from ether/CH_3CN/CH_2Cl_2 at room temperature. Single crystals with dimensions of 0.057 × 0.087 × 0.130 for **1** and 0.22 × 0.33 × 0.35 mm^3 for **2** were mounted on a nylon CryoLoop (Hampton Research) with Krytox Oil (DuPont) and centered on the goniometer of an Oxford Diffraction Xcalibur diffractometer equipped with a Sapphire 3 CCD detector. The data collection routine, unit cell refinement, and data processing were carried out with the program *CrysAlis*.[9]

The Laue symmetry of **1** was consistent with the triclinic space groups $P1$ and $P\bar{1}$. The centric space group $P\bar{1}$ was chosen. The structure was solved by direct methods using *SHELXS-86*[10] and refined using *SHELXTL NT*.[11] The asymmetric unit of the structure comprises a 0.5 crystallographically independent manganese complex, one CH_2Cl_2, and one CH_3CN. Residual electron density suggested substantial disorder of the TPA ligand, modeled as a two-position disorder with relative occupancies of 72.5 and 27.5%. There was also evidence of CH_2Cl_2 disorder, but efforts to model this disorder did not improve the overall model. The final refinement involved anisotropic displacement parameters for non-hydrogen atoms and a riding model for all of the hydrogen atoms. *SHELXTL NT* was used for molecular graphics generation.

For **2**, the Laue symmetry and systematic absences were consistent with the tetragonal space group $P4_22_12$. The structure was solved using *SIR92*[12] via the *WinGX* graphical interface,[13] and the structure was refined using *SHELXTL NT*. The asymmetric unit of the structure comprises one manganese ion, one TPA ligand, and one-quarter of each of two different TCNE dimer units. The final refinement model involved anisotropic displacement parameters for non-hydrogen atoms and a riding model for all of the hydrogen atoms. The structure was refined as an inversion twin giving BASF = 0.51(3). Both TCNE ligands are disordered. In one TCNE dimer, C25 is disordered across the Wyckoff *a* positions residing 50% of the time at x,y,z and $-x,-y,z$ and 50% of the time at $y,x,-z$ and $-y,-x,-z$, relative to the (0,0,0) special position. In the second TCNE dimer, C21 shows the same type disorder across the Wyckoff *b* positions. *SHELXTL NT* was used for molecular graphics generation. Crystal data, together with details of the diffraction experiment and subsequent calculation, are summarized in Table 1.

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Table 1. Crystal Data and Structure Refinement for **1** and **2**

	1·2CH$_3$CN·2CH$_2$Cl$_2$	**2**
empirical formula	$C_{66}H_{46}Mn_2N_{26}Cl_4$	$C_{24}H_{18}ClMnN_8O_4$
fw	1454.97	572.85
T (K)	100	100
cryst syst	triclinic	tetragonal
space group	$P\bar{1}$	$P4_22_12$
a (Å)	10.4432(17)	17.170(3)
b (Å)	12.2726(16)	17.170(3)
c (Å)	13.708(2)	17.1837(6)
α (deg)	88.505(12)	
β (deg)	75.560(14)	
γ (deg)	87.077(12)	
V (Å^3)	1698.9(4)	5065.9(13)
Z	1	8
D_{calcd} (mg/m^3)	1.422	1.502
μ (mm^{-1})	0.592	0.675
cryst dimensions (mm^3)	0.130 × 0.087 × 0.057	0.35 × 0.33 × 0.22
wavelength (Å)	0.71073	0.71073
R1^a [$I > 2\sigma(I)$]	0.0678	0.0418
wR2^b [$I > 2\sigma(I)$]	0.1525	0.1094

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [(F_o)^2 + 2(F_c)^2]/3$.

Results and Discussion

Air-sensitive complexes **1** and **2** were synthesized by a metathesis reaction between [Mn(TPA)(CH$_3$CN)$_2$](ClO$_4$)$_2$ and KTCNE; the products formed depending on the ratio of starting materials used. The goal was to prepare a corner building block for a molecular square (1:2 ratio of manganese to TCNE) or a complete molecular square (1:1 ratio). Although the isolated species do exhibit the intended ratio based on the starting materials, neither desired geometry was isolated.

The reaction of [Mn(TPA)(CH$_3$CN)$_2$](ClO$_4$)$_2$ with KTCNE in a 1:2 stoichiometric ratio gives rise to the formation of **1**. The presence of the two bridging μ_2-(TCNE)$_2^{2-}$ ligands and one terminal TCNE$^{\bullet/-}$ ligand was confirmed by X-ray crystal structure analysis (Figure 1) and supported by IR.[14] The manganese ions remain in the 2+ oxidation state.

The complex is seven-coordinate with the other four coordination sites being occupied by the TPA ligand. To the best of our knowledge, this is the first time that three TCNE radical anions have been found to be coordinated to one metal center. Such a structure would, in principle, be required for the formation of a molecular cube. However, it is clear that the description of the ligands as TCNE$^{\bullet/-}$ is only formally correct. The two bridging TCNE$^{\bullet/-}$ ligands are stacked to form a closed-shell dimer dianion, [μ_2-(TCNE)$_2^{2-}$]. We have observed and reported this species previously in another complex,[2] and Miller and co-workers have both observed it with main group cations and examined it theoretically.[15] It has also been reported in a dinuclear vanadium complex.[16] As before, the N−Mn−N bond angle involving the [μ_2-(TCNE)$_2^{2-}$] ligand is only about 76°, compared to an ideal angle of 90°. This distortion permits the π-type dimer of two TCNE radicals to form. The C−C bond distance in the dimer is 2.97 Å, which is comparable to previously observed values.[2] Whereas the third (nominally terminal) TCNE radical appears to be nondimerized, an examination of the packing diagram (Figure 2) shows that an equivalent interaction with nearly the same intermolecular C−C bond lengths (2.91 Å) exists between TCNE radicals on adjacent molecules.

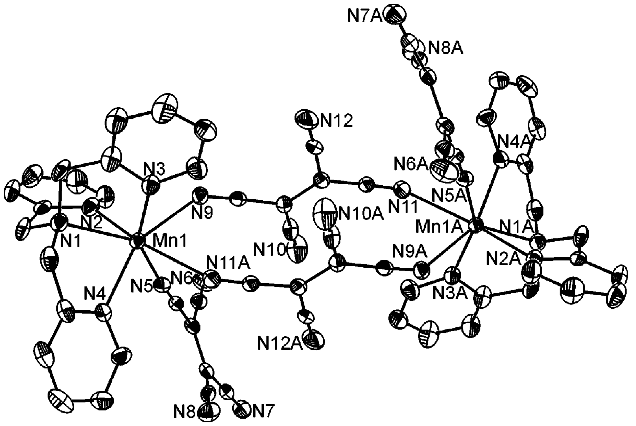

Figure 1. View of the coordination environments with major atom numbering scheme of the manganese atom in **1** with a 50% thermal ellipsoid probability. Solvent molecules and hydrogen atoms are omitted for clarity.

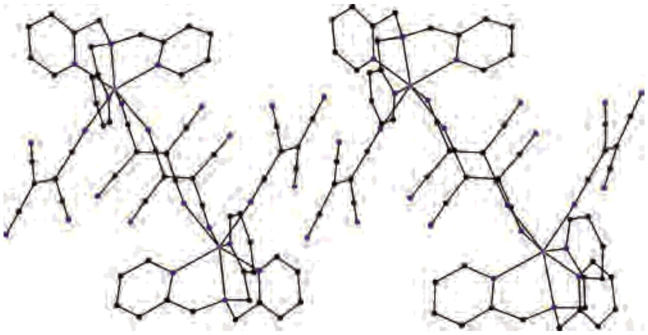

Figure 2. Packing diagram of **1** showing intermolecular π interactions between terminal TCNE radical anions, forming a 1D zigzag infinite stack along the *c* axis.

Thus, the structure is essentially an infinite chain of dinuclear species. This type of interaction has not previously been observed intermolecularly and indicates the apparent strong tendency for two TCNE$^{\bullet/-}$ to dimerize and consequently pair the unpaired electrons.

The plots of χT versus T and χ^{-1} versus T for **1** are shown in Figure 3. The data do not conform exactly to the Curie−Weiss law, although the behavior is fairly consistent with χT expected for two uncoupled spin-only Mn(II) centers, 8.75 emu·K/mol. The interpretation we favor is that the unpaired electrons on the organic radicals are essentially quenched (very strongly antiferromagnetically coupled) at low temperature, and therefore do not contribute to χT.

However, at higher temperatures, there are thermal excitations within the organic part of the complex that would create additional spins as the temperature is raised, causing χT to continue to increase slowly rather than level off. The slight downturn of the χT data at low temperature supports the idea of a weak antiferromagnetic interaction between the Mn(II) centers. Notably, this interpretation means that the unpaired electron on the terminal TCNE radical is also strongly

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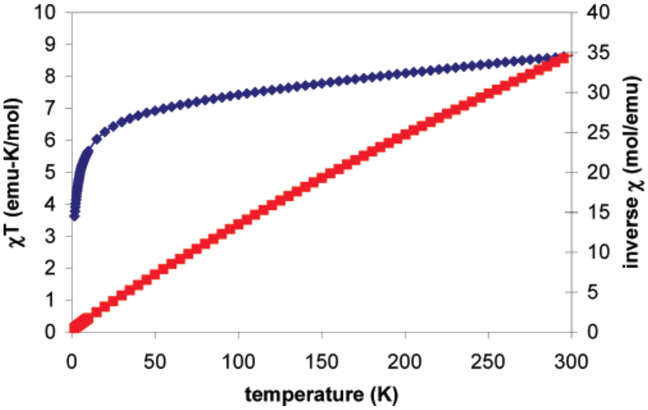

Figure 3. Temperature dependence of χT (♦)and χ^{-1} (■) for **1** measured in 5000 G.

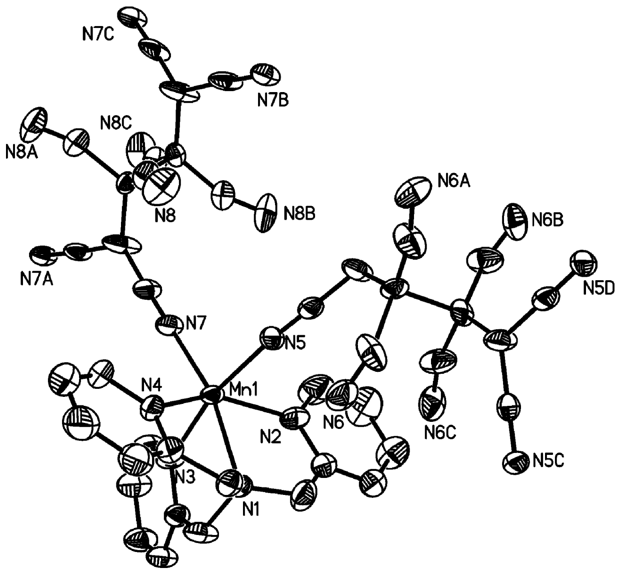

Figure 4. View of coordination environment of the manganese atom in **2.** The TCNE dimers are modeled as being disordered over two symmetry positions.

antiferromagnetically coupled to its equivalent ligand on an adjacent molecule such that it too does not contribute significantly to the magnetic properties at room temperature. The most important conclusion from this data is that not only are the organic radicals not magnetically active, but we see no evidence for net ferromagnetic coupling of the two manganese centers, as would be required for long-range magnetic order in the vanadium TCNE magnet.

The reaction of $[\mathrm{Mn(TPA)(CH_3CN)_2](ClO_4)_2}$ with KTCNE in a 1:1 stoichiometric ratio affords **2** formulated as $[\mathrm{Mn(TPA)}(\mu_4\text{-}\mathrm{C_4(CN)_8})_{0.5}]\cdot\mathrm{ClO_4}$. The crystal structure of this compound (Figure 4) again contains a tetradentate TPA ligand and illustrates another way that two TCNE radical anions can pair their electrons. In this case, a six-coordinate manganese(II) center is in a pseudo-octahedral environment with two cis coordination sites occupied by two different octacyanobutyl dianions.

In this structure, the TCNE radicals are dimerized via a carbon−carbon σ bond (rather than the four-center, two-electron bond), yielding a species that has been previously characterized structurally and spectroscopically.[14] As with one of the two compounds in the sole previous report, the dianion here is disordered so that a meaningful comparison of bond lengths and angles is not possible. Like both examples previously reported, the four terminal CN moieties in the present compound each coordinate to a metal center to form a ribbon polymer (Figure 5).[3]

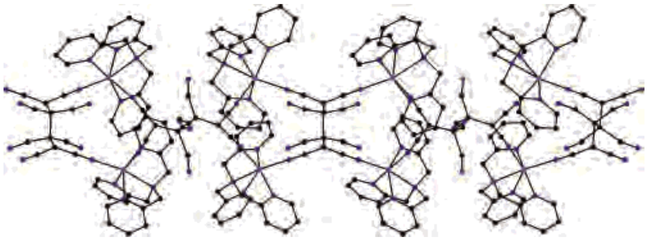

Figure 5. View of the 1D ribbon architecture in **2** along the *c* axis. Perchlorate anions and hydrogen atoms are omitted for clarity.

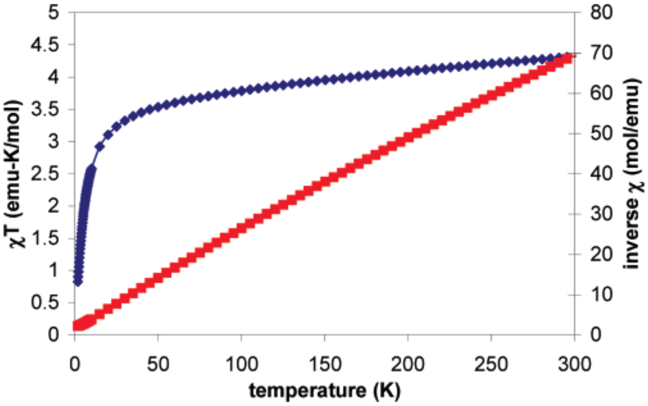

Figure 6. Temperature dependence of χT (♦) and χ^{-1} (■) for **2** measured in 5000 G.

Compound **2** also shows a temperature-dependent magnetic behavior similar to that of **1** and roughly obeys the Curie−Weiss law between 1.8 and 300 K, affording $C = 4.3$ emu·K/mol and $\theta = -9.8$ K (Figure 6). Note that the data for **2** are expressed as per manganese center, whereas for **1**, they are per two manganese centers. At room temperature, the χT value is 4.32 emu·K/mol for **2**, close to that calculated for high-spin Mn^{2+} with $S = {}^5/_2$ (4.375 emu·K/mol), demonstrating that, as expected, $[\mu_4\text{-}\mathrm{C_4(CN)_8}]^{2-}$ does not contribute to the total magnetic susceptibility. Upon cooling, the χT value decreases slowly, indicating that, like for **1**, only weak antiferromagnetic coupling between the Mn(II) centers exists.

It is clear from the above results that the dimerization motifs we observe in the above compounds are simply variations on a theme. In **1**, we observe a four-center, two-electron π-type bond, and in **2**, we observe the formation of a more conventional σ bond. Yet, the effects of this pairing are essentially the same: strong antiferromagnetic coupling due to the formation of bonds quench the unpaired electrons on all of the $\mathrm{TCNE}^{\bullet/-}$ ligands to yield diamagnetic species that are incapable of mediating ferromagnetic coupling between coordinated metal centers.

Conclusions

Two manganese(II) coordination complexes have been prepared with the intention of having them possess TCNE radical anions as ligands. In both cases, dimerization of the radicals results in quenching of the spin due to the formation of either a four-center two-electron bond or a carbon–carbon σ bond. The magnetic properties of these compounds are characteristic of five unpaired electrons associated with the high-spin d^5 transition metal with no significant contribution from the organic radicals. Furthermore, only weak antiferromagnetic coupling between the transition metals was observed.

The possible importance of these results stems from the observation that magnetic phases analogous to V[TCNE]$_2$, but based on other transition metals, have much lower T_c's.[17] The discovery of an air-stable room-temperature molecule-based magnet would be of great importance, and compounds based on metals other than V(II) would seem to be required. Miller and co-workers have recently reported a powder diffraction structure of a magnetic iron network with bridging TCNE radical anions that orders at 90 K.[18] But another reason for the lower ordering temperatures in non-V(II) solids might the greater concentration of (magnetically ineffective) bridging dimer dianions relative to bridging radical anions in the network, then reducing or eliminating dianion bridges would presumably increase T_c. This might be achieved by replacing TCNE with an electron acceptor that is less likely to dimerize as a result of the presence of steric bulk. We are pursuing just such a strategy.

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Supporting Information Available: X-ray crystallographic details (in CIF format) for [Mn(TPA)(TCNE)]$_2$[μ_2-(TCNE)$_2$], (**1**) and [Mn(TPA)(μ_4-C$_4$(CN)$_8$)$_{0.5}$]·ClO$_4$, (**2**). This material is available free of charge via the Internet at http://pubs.acs.org.

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