Articles

Weak Effect on T_c with Increased Interchain Distances. Structure and Magnetic Properties of (*meso*-Tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphinato)manganese(III) Tetracyanoethenide, [Mn^{III}TP′P]$^+$[TCNE]$^{•-}$ [†]

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(*meso*-Tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphinato)manganese(III) tetracyanoethenide, [MnTP′P][TCNE], has been structurally and magnetically characterized. [MnTP′P][TCNE] ($C_{96}H_{108}MnN_8O_4$) belongs to the triclinic $P\bar{1}$ (No. 2) space group with a = 8.597(2) Å, b = 14.756(4) Å, c = 17.573(5) Å, α = 101.16 (2)°, β = 100.56-(2)°, γ = 96.37(2)°, and Z = 1. Due to the oxidative instability of the phenoxy groups, [Mn^{III}TP′P][TCNE] was prepared from the reaction of [Mn^{III}TP′P]OAc with the strong acid H_2TCNE (pK_a = 3.6) in the presence of TCNE to form acetic acid and the product. [MnTP′P][TCNE] is a coordination polymer with the Mn(III) sites bridged by *trans*-μ_2-bound [TCNE]$^{•-}$ with relatively short (8.587 Å) intrachain and long ($\geq$14.756 Å) interchain Mn$\cdots$Mn separations. The magnetic data above 210 K obey the Curie−Weiss expression with an effective Θ value of 90.0 K, the largest yet reported for a soluble molecule-based magnet. In addition to a 15 K T_c hysteretic behavior with a coercive field of 100 Oe is observed at 5 K. Despite the significant steric bulk leading to the substantially decreased interchain interactions that are crucial for magnetic ordering, the T_c is unexpectedly high and suggests that other linear chain systems may be expected to exhibit magnetic ordering at higher temperatures.

Introduction

The preparation and characterization of molecule-based magnetic materials is a growing area of increasing contemporary interdisciplinary research.[2,3] The electron-transfer salt [FeCp*$_2$]$^{•+}$[TCNE]$^{•-}$ (Cp* = pentamethylcyclopentadienide; TCNE = tetracyanoethylene) with a Curie (critical or ordering) temperature, T_c, of 4.8 K was the first bulk molecular ferromagnet reported.[4] Subsequently, [MnCp*$_2$]$^+$[TCNQ]$^{•-}$ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane) and [MnCp*$_2$]$^+$[TCNE]$^{•-}$ have been reported to have T_cs of 6.2[5] and 8.8 K,[6] respectively. Extension of the latter reaction to the V(C$_6$H$_6$)$_2$$^•$ donor, which is isoelectronic to MnCp*$_2$$^•$, led to the isolation of a disordered, infusible V(TCNE)$_x$·y(solvent) magnet with a T_c exceeding room temperature; *i.e.*, $T_c \sim$ 400 K.[7]

Subsequently, a new structure type exemplified by [MnTPP]$^+$[TCNE]$^{•-}$ (TPP = *meso*-tetraphenylporphinato) was reported to exhibit bulk magnetic properties.[8] [MnTPP]$^+$[TCNE]$^{•-}$ is an extended linear chain (1-D) complex that was characterized to be a ferrimagnet with a T_c of 16 K

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[determined from scaling analysis of the magnetization as a function of temperature and magnetic field, and also ac susceptibility (vide infra)], and its magnetic susceptibility, χ, can be fit to the Curie–Weiss expression, $\chi \propto (T - \Theta)^{-1}$ between 115 and 250 K ($\Theta = +61$ K).[8] With the objectives of elucidating the importance of 1-D interactions with respect to 3-D interactions, establishing the structure–function relationship for this new class of materials, as well as characterizing new molecule-based magnets with enhanced T_cs and θs, we have pursued the study of this class of compounds.

Due to the relative ease of modifying the porphyrin structure we purposely sought to substantially increase the one-dimensionality (1-D) of the system by increasing the interchain separations with respect to [MnTPP][TCNE] by introducing a pair of bulky *tert*-butyl groups on each phenyl ring. For linear chain magnets Θ is proportional to the intrachain exchange coupling $J_{\parallel}$. It is well established that, except at absolute zero, long range order cannot occur for a 1-D system.[9] Since T_c is proportional to the geometrical average of intra- and interchain exchange, $J_{\parallel}$ and $J_{\perp}$, respectively, which in turn are inversely proportional to the separation r between spin sites generally as r^{-n} (*e.g.*, $n \geq 6$ for situations where superexchange pathways dominate),[10] small increases in r should have a dramatic effect on T_c and Θ. Since [MnTPP][TCNE] is comprised of parallel 1-D chains, and the spin density on [MnTPP]$^+$ resides in the porphyrin plane[11] and not on the four phenyl rings twisted out of conjugation with the porphyrin plane, then, assuming a similar structure is formed, the increased steric demand on the substituted phenyl rings should increase the interchain separation between the spins and decrease $J_{\perp}$. The decrease in $J_{\perp}$ should be observed as a decrease in T_c. If, however, only the intrachain (1-D) orbital interactions are important, the increased interchain separations should have only a minor influence on T_c. Therefore, T_c and Θ should be comparable to those observed for [MnTPP][TCNE]. Herein we report the structure and magnetic properties of (*meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphinato)manganese(III) tetracyanoethenide, [MnTP′P]$^+$[TCNE]$^{\bullet-}$·2PhMe.
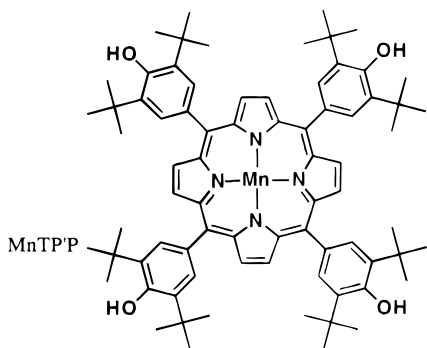
We also describe a convenient, new method to prepare radical ion salts of metalloporphyrins containing redox-active substituents, which are not accessible via the classical route of direct electron transfer between the porphyrin donor and the neutral acceptor.

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Table 1. Crystallographic Details for [Mn^{III}TP′P][TCNE]·2MePh

chem formula: $C_{96}H_{108}MnN_8O_4$	formula mass = 1492.92 Da
$a = 8.597$ (2) Å	space group: $P\bar{1}$ (No. 2)
$b = 14.756$ (4) Å	$T = -65$ °C
$c = 17.573$ (5) Å	$\lambda = 0.710\ 690$ Å
$\alpha = 101.16$ (2)°	$\rho_{calcd} = 1.166$ g cm^{-3}
$\beta = 100.56$ (2)°	$\mu = 2.01$ cm^{-1}
$\gamma = 96.37$ (2)°	$R(F_o)^a = 0.078$
$V = 2125.1$ Å^3	$R_w(F_o)^b = 0.074$
$Z = 1$	

$^a \Sigma\ (|F_o| - |F_c|)/\Sigma|F_o|.\ ^b \Sigma\ w(|F_o| - |F_c|)^2/\Sigma\ w|F_o|^2.$

Table 2. Selected Interatomic Distances, Å, for [Mn^{III}TP′P][TCNE]·2MePh

Mn(1)−N(3)	2.299(10)	N(11)−C(15)	1.388(7)
Mn(1)−N(11)	1.988(5)	N(12)−C(10)^a	1.391(7)
Mn(1)−N(12)	1.998(4)	N(12)−C(17)	1.387(7)
N(2)−C(2)	1.068(12	C(1)−C(1)^b	1.378(27)
N(3)−C(3)	1.000(21	C(1)−C(2)	1.370(24)
N(11)−C(12)	1.413(7	C(1)−C(3)	1.317(37)

^{a} $1 - x, 1 - y, 1 - z.$ ^{b} $2 - x, 1 - y, 1 - z.$

Table 3. Selected Intramolecular Angles (deg) for [Mn^{III}TP′P][TCNE]·2MePh

N(2)−C(2)−C(1)	172(3)	C(1)^a−C(1)−C(2)	135(4)
N(3)−C(3)−C(1)	155(2)	C(1)^a−C(1)−C(3)	97(3)
Mn(1)−N(3)−C(3)	129(1)	C(2)−C(1)−C(3)	128(2)

^{a} $2 - x, 1 - y, 1 - z.$

Experimental Section

Synthesis. All manipulations were carried out under an atmosphere of nitrogen using standard Schlenck techniques or in a Vacuum Atmospheres glovebox under nitrogen. Solvents used were predried and distilled from appropriate drying agents. H$_2$TP′P was prepared by a literature method.[12] [Mn^{III}TP′P][OAc] was prepared from H$_2$TP′P and Mn(OAc)$_2$ utilizing the below modified literature method.[13]

[Mn^{III}TP′P]$^+$[OAc]$^-$. Mn(OAc)$_2$·4H$_2$O (0.735 g; 3 mmol) was added in one portion to a solution of (1.127 g; 1 mmol) H$_2$TP′P and 1 g of NaOAc in 150 mL of hot glacial acetic acid, and the mixture was allowed to reflux for 10 min. Because the UV spectrum taken from an aliquot in CHCl$_3$ revealed an incomplete conversion, another 0.2 g of Mn(OAc)$_2$·4H$_2$O was added, and reflux was continued for an additional 10 min. When the UV spectrum indicated the conversion of the entire free base, the now deep green solution was allowed to cool down to room temperature and then poured into 400 mL of H$_2$O. The dark green precipitate formed was filtered off, washed with H$_2$O, air-dried, dissolved in a minimal amount of MeOH, poured into 300 mL of a saturated NaOAc-solution, filtered off and air-dried again, dissolved in 300 mL of CHCl$_3$, dried over NaOAc, evaporated to dryness, and recrystallized from CHCl$_3$/petroleum ether to yield 1.05 g (84%) of the desired product as dark green crystals.

[Mn^{III}TP′P]$^+$[TCNE]$^{\bullet-}$·2MePh. H$_2$TCNE[14] (6.5 mg; 0.05 mmol) dissolved in 20 mL of THF was added in one portion to a stirred solution of (24 mg; 0.1 mmol) [Mn^{III}TP′P][OAc] and (6.5 mg; 0.05 mmol) TCNE in 60 mL of toluene/THF (1:1) at room temperature under nitrogen. The mixture was heated to reflux, and the solvent was slowly removed under reduced pressure. When the reaction mixture was brought nearly to dryness, one observed a slight change in color from green to black-green, and the odor of free HOAc could be detected in the removed solvent. Recrystallization of the residue from toluene/hexane and drying under vacuum yielded 97 mg (65%) of the radical ion disolvate salt as a black-green powder. IR (Nujol): $\nu_{C\equiv N}$

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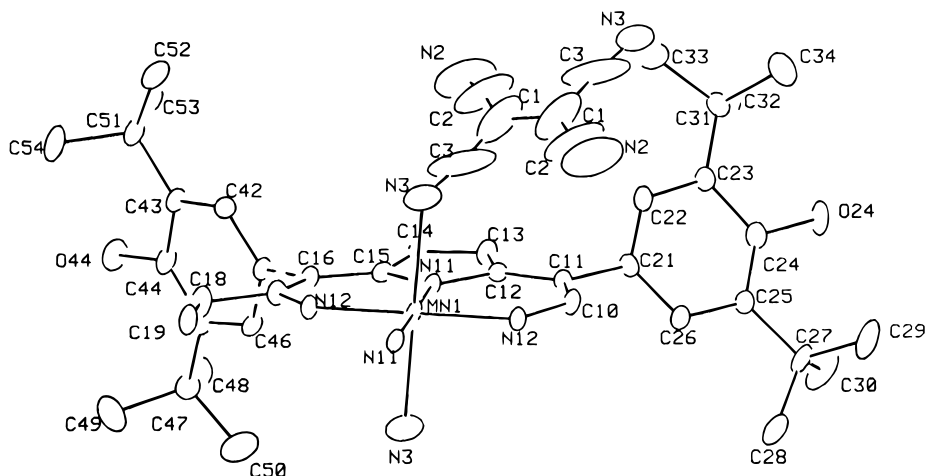
Figure 1. ORTEP (20%) atom labeling diagram for centrosymmetic [MnTP′P]⁺[TCNE]•⁻ showing half of a cation and the anion. Note the large thermal motions on the [TCNE]•⁻.
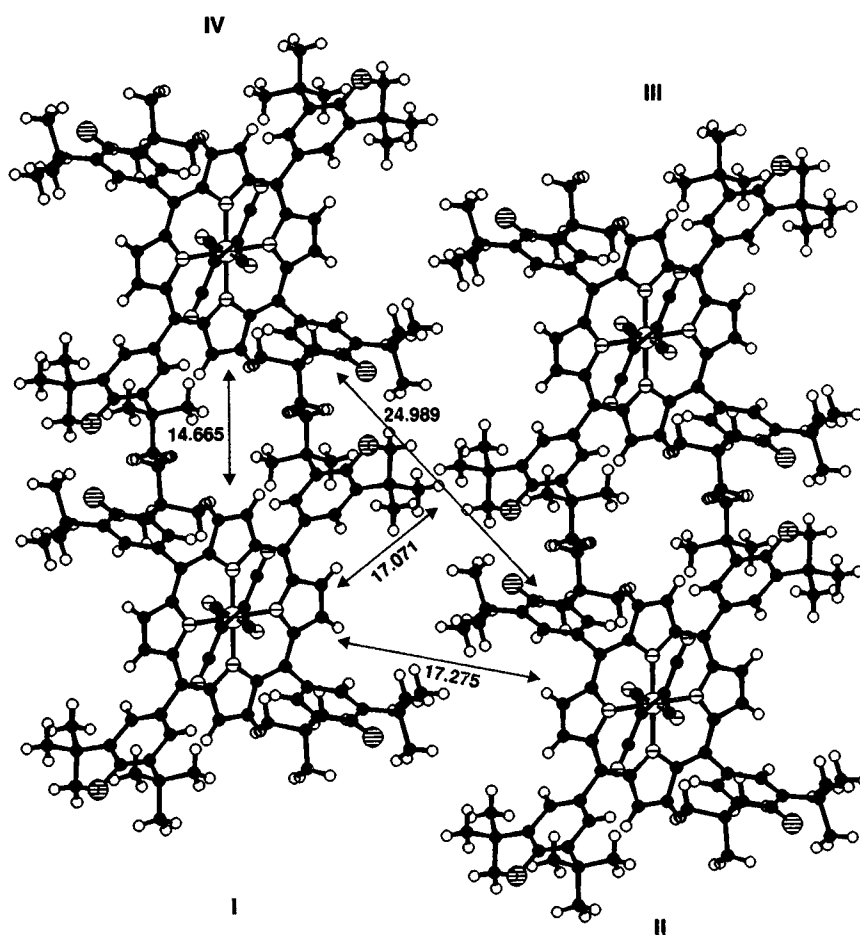
Figure 2. View normal to the unique chains **I−IV** for [MnTP′P][TCNE]·2PhMe.

absorptions at 2133 s and 2197 m cm⁻¹. Anal. Calcd for the disolvate $C_{96}H_{108}N_8O_4Mn$ (found): C, 77.24 (77.57); H, 7.29 (7.24); N, 7.51 (8.10).

X-ray Structure Determination. Crystals of the ditoluene solvate suitable for single-crystal X-ray diffraction were obtained by refrigerating a toluene/diethyl ether solution. Cell constants and an orientation matrix for the data collection were obtained by the standard methods from 25 reflections at −65 °C. Systematic absences and subsequent least-squares refinement were used to determine the space groups. During data collection the intensities of several representative reflections were measured as a check on crystal stability. Where there was a loss of intensity during data collection, an isotropic decay correction (<3%), was applied. Equivalent reflections were merged and only those for which $(F_o)^2 > 3\sigma(F_o)^2$ were included in the refinement, where $\sigma(F_o)^2$

is the standard deviation based on counting statistics. Data were also corrected for Lorentz and polarization factors. An absorption correction of 2.01 cm⁻¹ was used. Crystallographic details are summarized in Table 1 and tables of the atomic coordinates, anisotropic thermal parameters, and bond angles are provided as Supporting Information. Selected bond distances and angles are listd in Tables 2 and 3, respectively. The toluenes were modeled with 10 isotropic atoms "head-to-toe" disorder with appropriate full weighted and half-weighed occupancies.

Magnetic Measurements. The 1.4−300 K magnetic susceptibility was determined on a Faraday magnetometer[15] or a Quantum Design MPMS SQUID magnetometer system. The ac magnetic susceptibility was determined in the range of 1 Hz to 10 kHz using a Quantum Design PPMS-9AC 9T ac/dc magnetometer above 1.9 K.
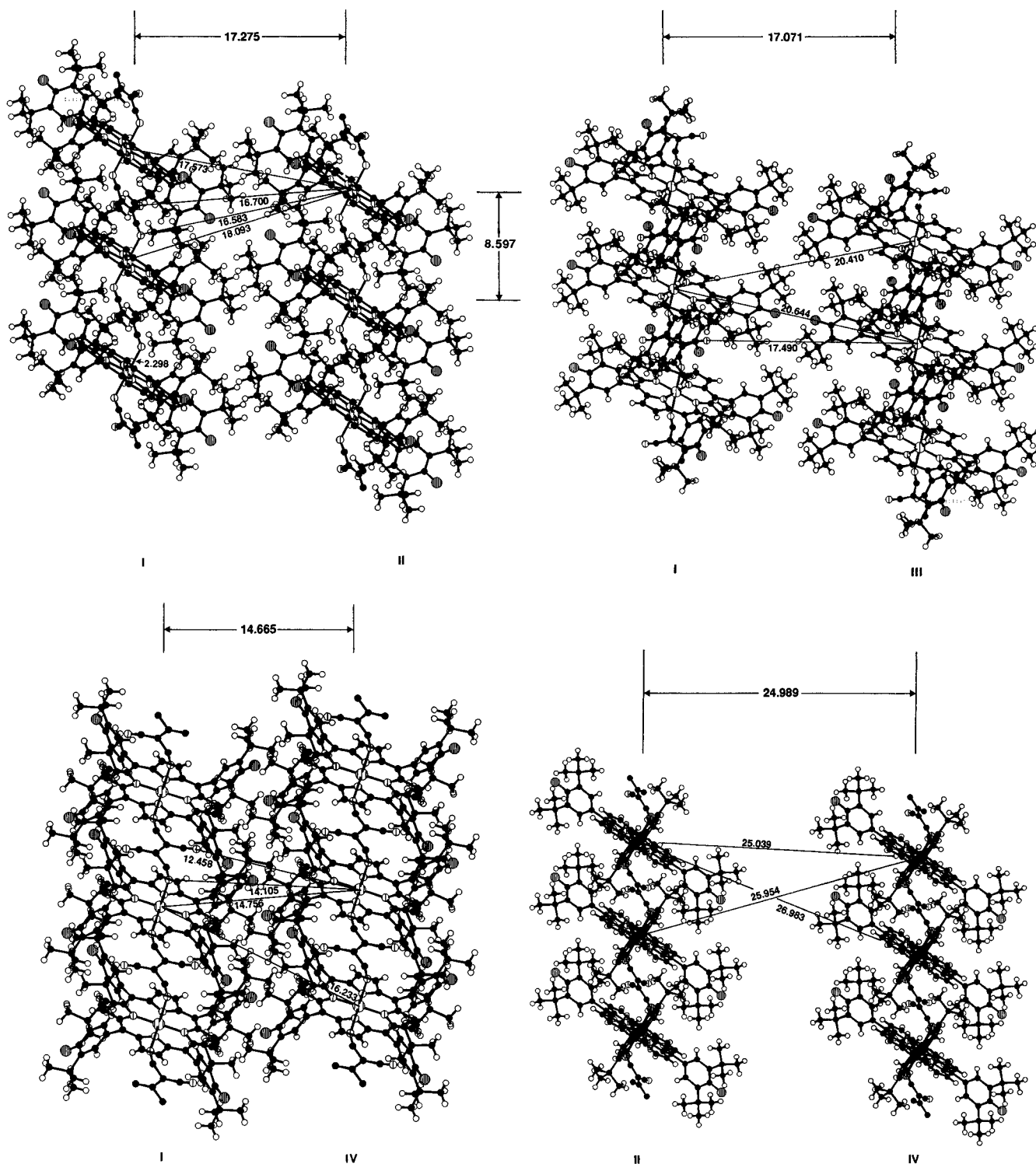
Figure 3. View of intra- and interchain interaction among the unique chains: **I**, **II**, **III**, and **IV** for [MnTP′P][TCNE]·2PhMe. Note the [TCNE]•⁻ *trans-μ₂-N-σ*-bonding to [MnTP′P]⁺ and the uniform chains. The toluenes of solvation are not shown for clarity.

Results and Discussion

Mn^{II}TP′P could not be synthesized from available [Mn^{III}-TP′P]X (X = Cl, Br, OAc) by the literature method given for MnTPP[8,16] due to the instability of the hydroxy-substituents against reducing agents like NaBH₄; in addition, all attempts to prepare MnTP′P directly from the free base failed. The desired product, [Mn^{III}TP′P]⁺[TCNE]•⁻, was thus prepared by the direct exchange of the axial ligand [OAc]⁻ in [MnTP′P]-[OAc] utilizing an acid-base reaction between the strong acid tetracyanoethane (H₂TCNE) (pK_a = 3.6)[14] and the acetate ion (pK_b = 9.25) in the presence of neutral TCNE, eq 1.

$$2[Mn^{III}TP'P]^+[OAc]^- + H_2TCNE + TCNE \rightarrow$$
$$2HOAc + 2[Mn^{III}TP'P]^+[TCNE]^{\bullet-} \quad (1)$$
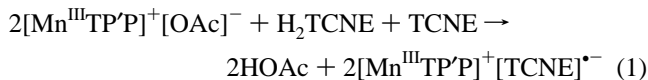
The structure determination of [Mn^{III}TP′P]⁺[TCNE]•⁻·2PhMe reveals a [TCNE]•⁻ with high thermal motions on the C's and

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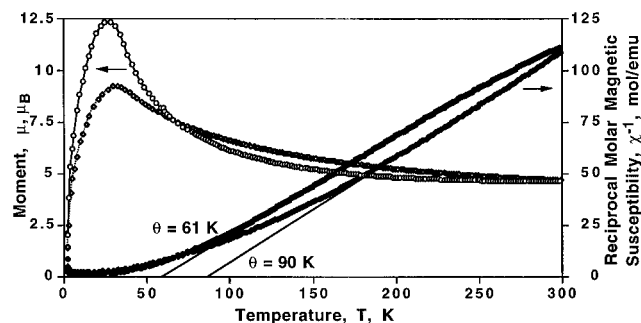
Figure 4. Reciprocal molar magnetic susceptibility, χ^{-1}, and moment, μ, as a function of temperature for polycrystalline [Mn^{III}TPP]$^+$[TCNE]$^{•-}$·2MePh (O, ●)[8] and [Mn^{III}TP′P]$^+$[TCNE]$^{•-}$·2MePh (△, ◇). The moment is $(8\chi T)^{1/2}$ where χ is taken as $M(0.5 \text{ T})/0.5 \text{ T}$.

N's nonbonded to the Mn's, Figure 1. The (NC)$_2$C−C(CN)$_2$ distance of 1.378 (27) Å is comparable to the distance reported for isolated [TCNE]$^{•-}$ in [FeCp*$_2$][TCNE] (*i.e.*, 1.392)[17] or 1.369 Å for [TCNE]$^{•-}$ *trans-μ_2-N-σ-bound* to Mn in [MnTPP]$^+$[TCNE]$^{•-}$,[8] but due to the large esd arising from the large thermal motion, it is not uniquely distinct from the 1.344, 1.49, and 1.478 Å distances reported for TCNE^0, isolated [TCNE]$^{2-}$ in {[CoCp*$_2$]$^+$}$_2$[TCNE]$^{2-}$,[17] and [TCNE]$^{2-}$ *trans-μ_2-N-σ-bound* to Ir in [(Ph$_3$P)$_2$(OC)Ir]$_2$[TCNE].[18] [TCNE]$^{•-}$ is essentially planar with a 6.2° twist; this is larger than the 1.9° twist for [MnTPP]$^+$[TCNE]$^{•-}$.[8]

The $\nu_{C\equiv N}$ absorptions at 2133 s and 2197 m cm^{-1} (Nujol) confirm the presence of [TCNE]$^{•-}$ and are inconsistent with [TCNE]^n ($n = 0, 2-$).[18] These values are only slightly shifted from the 2147 m and 2192 s cm^{-1} values reported for [MnTPP]-[TCNE].[8]

The [MnTP′P]$^+$ cation is comparable to other metallo-*meso*-tetraphenylporphinato complexes with it being essentially planar with the Mn-N distances averaging 1.993 Å. The solid state motif comprises 1-D ···D$^+$A$^{•-}$D$^+$A$^{•-}$··· chains (D = MnTP′P; A = TCNE) where the [TCNE]$^{•-}$ is *trans-μ_2-N-σ-bound* to Mn at a distance of 2.299(10) Å, the Mn−N−C angle is 129(1)°, and the angle between the mean-planes of [MnTP′P]$^+$ and [TCNE]$^{•-}$ is 30.4°. The separation is comparable to that observed for [MnTPP][TCNE]·2PhMe [2.305(4) Å],[8] but the angle is substantially reduced from the 148.1 (4)° reported for [MnTPP][TCNE]·2PhMe,[8] Figures 2 and 3. The intra- and interchain Mn···Mn separations for [MnTP′P][TCNE]·2PhMe and [MnTPP][TCNE]·2PhMe are presented in Figure 2.

The key intrachain Mn···Mn separation is 8.587 Å which, due to the canting of the porphyrin planes, is 15% shorter than the 10.116 Å observed for [MnTPP][TCNE]·2PhMe[8] coincident with enhanced 1-D coupling ($J_\parallel$) as evidenced from the Θ value obtained from the magnetic data (*vide infra*). In contrast, the interchain Mn···Mn separations are substantially larger than observed for [MnTPP][TCNE], *i.e.*, the three shortest are 14.756, 16.233, and 17.573 Å as compared to 11.006, 11.823, and 13.269 Å for [MnTPP][TCNE]. Since the 3-D ordering temperature, T_c, is a strong function of the interchain interactions, the larger distances suggest that a significantly reduced T_c which is not in accord with experimental data (*vide infra*).

The 1.4−300 K reciprocal of the corrected magnetic susceptibility, χ^{-1}, and moment, μ, of [MnTP′P][TCNE] and [MnTPP]-[TCNE] are presented in Figure 4. Above ca. 210 K the susceptibility of [MnTP′P][TCNE] can be fit by the Curie−Weiss expression, $\chi \propto 1/(T - \Theta)$, with an effective Θ of 90.0 K; the average of 12 determinations ranging from 85.2 to 92.2
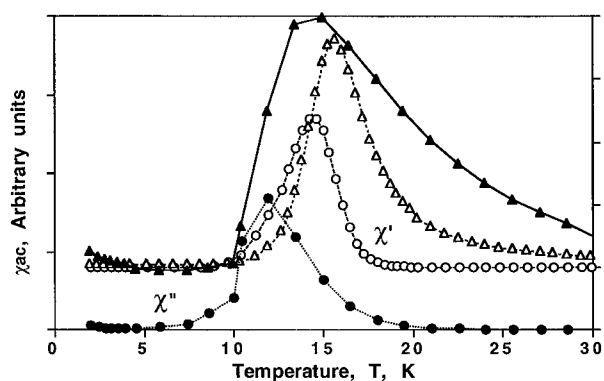

Figure 5. Real, χ' (△, ▲), and imaginary ac susceptibly, χ'' (O, ●), as a function of temperature taken at 10^4 Hz at a 0.012 Oe dc and a 10 Oe applied field ac for polycrystalline [Mn^{III}TP′P]$^+$[TCNE]$^{•-}$ (●, ▲) and [Mn^{III}TPP]$^+$[TCNE]$^{•-}$ (O, △).

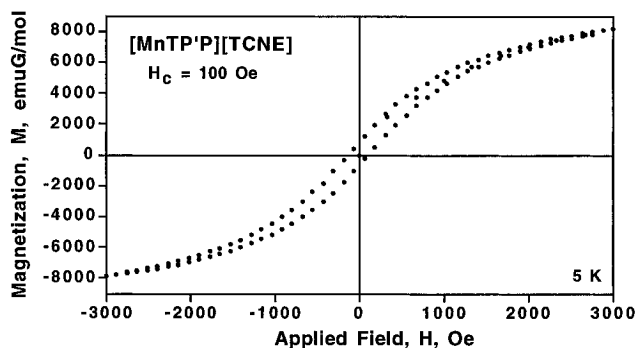**Figure 6.** Magnetization, M, as a function of applied field, H, at 5 K showing hysteresis with a coercive field, H_c, of 100 Oe for [Mn^{III}TP′P]$^+$[TCNE]$^{•-}$.

K. This is significantly exceeds the effective +61 K Θ-value obtained between 115 and 250 K for [MnTPP][TCNE],[8] and is consistent with the 15% shorter intrachain separations. The 90 K Θ-value is the largest effective Θ-value reported for any molecule-based magnet. The observed room-temperature effective moment, μ_{eff} [$\equiv (8\chi T)^{1/2}$], averages 4.90 μ_B which is slightly reduced from the value of 5.12 μ_B reported for [MnTPP]-[TCNE] and the expectation of 5.20 μ_B for isotropic independent $g = 2\ S = 2$, and $S = \frac{1}{2}$ radicals. A minimum in the value of χT as a function of temperature, characteristic of 1-D ferrimagnetic behavior,[19] is not observed; presumably it occurs at or above room temperature. Hence, the observed Θ-value is considered only as an effective Θ. Nonetheless, ferrimagnetic behavior is evident from the saturation magnetization. The 5 K saturation magnetization is 16 000 emu G/mol in accord with the expectation of antiferromagnetic coupling, *i.e.*, 16 755 emu G/mol for the $S_{Tot} = 2 - \frac{1}{2}$ system, which is substantially lower than expected for ferromagnetic coupling, *i.e.*, 27 925 emu G/mol for the $S_{Tot} = 2 + \frac{1}{2}$ system.

The real part of the zero field ac magnetic susceptibility, $\chi'(T)$, has a maximum at 15 K for a frequency of 10 kHz, only 1 K lower than for the same data for [MnTPP][TCNE]. Similarly the imaginary part of the zero field ac magnetic susceptibility, $\chi''(T)$, has a maximum only 1 K lower than observed for [MnTPP][TCNE], Figure 5. These data suggest that T_c of [MnTP′P][TCNE] is only 1 K lower than that of [MnTPP][TCNE].[20] This is surprising in view of a greater than 33%

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increase in the interchain separations. Assuming $J_\perp \propto r^{-6}$, a 5-fold reduction of $J_\perp$ together with significant drop in T_c would be expected for this lattice expansion. Hysteresis with a coercive field, H_c, of 100 Oe is observed at 5 K, Figure 6. A more detailed analysis based upon extensive $M(H,T)$ data and more sophisticated physical models analyses is in progress.

Conclusion

[MnTP′P][TCNE] is a second example of a molecular-based magnetic material containing *trans-μ_2-N-σ*-bonded [TCNE]$^{\bullet-}$ subunits. Our results presented here suggest that the ferrimagnetic behavior of the parent compound [MnTPP][TCNE] is not unique, but reflects intrinsic properties of a whole class of structurally related compounds, which in turn are tunable by systematic variation of the porphyrin macrocycle. More importantly, the results of the magnetic measurements on [MnTP′P][TCNE] in comparison to the data obtained for [MnTPP][TCNE][8] indicate that the importance of *obvious* 3-D

interactions for long-range magnetic order might be overestimated.

Supporting Information Available: Tables giving a summary of the crystallographic data, fractional coordinates and and isotropic thermal parameters, anisotropic thermal parameters, bond distances and angles, and intramolecular nonbonding distances for [MnTP′P][TCNE]·2PhMe (15 pages). Ordering information is given on any current masthead page.

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