Structure and Magnetic Properties of Tetrakis(3,4,5-trimethoxyphenyl)porphinatomanganese(III) 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethenide: The First Example of an Isolated $[TCNQF_4]^{\bullet -}$

Mitchell T. Johnson,[a] Atta M. Arif,[a] and Joel S. Miller*[a]

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The crystal structure of *meso*-tetrakis(3,4,5-trimethoxyphenyl)porphinatomanganese(III) 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethenide, $[MnT(MeO)_3PP][TCNQF_4]\cdot 3$-($o$-$C_6H_4Cl_2$), $\mathbf{1}\cdot 3C_6H_4Cl_2$, provides the first example of a nondimeric $[TCNQF_4]^-$ that is stabilized by *trans*-μ-coordination to Mn^{III}. Compound $\mathbf{1}\cdot 3C_6H_4Cl_2$ crystallizes in the monoclinic $C2/c$ space group [a = 16.9486(10) Å, b = 25.7170(14) Å, c = 19.4009(12) Å, β = 107.091(4)°, V = 8082.8(8) Å^3, T = 200 K, Z = 4, $R(F_o)$ = 0.0547]. The $[TCNQF_4]^-$ formulation was confirmed from the crystal structure data, as well as the ν_{CN} absorption at 2196 and 2165 cm^{-1} in the IR spectrum. The $[TCNQF_4]^-$ moiety is planar with a methylene-carbon–ring-carbon distance of 1.41 Å, which is 0.038 Å longer than that for $TCNQF_4$. $\mathbf{1}\cdot 3C_6H_4Cl_2$ forms 1-D zigzag chains of alternating $\mathbf{1}^+$ and $[TCNQF_4]^-$, where the Mn^{III} atoms are bound in a *trans*-μ-fashion with Mn–N and intrachain Mn···Mn distances of 2.321(3) Å and 12.685 (4) Å, respectively. The MnNC angle and the dihedral angle between the $[TCNQF_4]^-$ and the mean MnN_4 planes are 135.9(2)° and 46.4°, respectively, with the phenyl rings rotated 80° with respect to the mean porphyrin plane. The magnetic susceptibility of $\mathbf{1}\cdot 2.3C_6H_4Cl_2$ can be calculated from the Curie–Weiss expression with θ = –37 K (T > 250 K) and θ′ = +29 K (75 < T < 200 K) with an observed minimum in $\chi T(T)$, typical of ferrimagnets, at 215 ± 10 K. At 2 T the magnetization is 14.900 emuOe/mol or 89% of 16.755 emuOe/mol expected for an S_{Tot} = 2 – 1/2 = 3/2 system. The intrachain antiferromagnetic coupling, J/k_B, is –71 K (–49 cm^{-1}; –61 meV) based on a fit to the Seiden expression for noninteracting chains comprised of alternating quantum (S = 1/2) and classical (S > 1/2) spins, and the Hamiltonian $H = -2JS_a\cdot S_b$. Compound $\mathbf{1}\cdot 2.3C_6H_4Cl_2$ ferrimagnetically orders at 7.3 K [based on the maxima in the 10 Hz χ′(T) data]. Hysteresis is observed at 2 K with coercive field, H_{cr}, of 17.1 kOe and remnant magnetization of 7.200 emuOe/mol; hysteresis is not observed at 5 K. This compound also displays metamagnetic behavior at 2 K above a critical field of 20.2 kOe. The frequency-dependent transitions observed in the χ′(T) and χ"(T) a.c. data are attributed to the transition to a spin glass or superparamagnetic state.

Introduction

Magnetically ordered molecular solids continue to attract attention worldwide, with a focus on new means of attaining a high degree of connectivity between spin-containing moieties.[1] Two classes of organic-based magnets exist; those with active and those with passive organic ligands. Passive organic ligands position the metal-ion-based spin sites to modulate the spin exchange, while active organic ligands contribute spins to the magnetic moment in addition to positioning the metal-ion-based spin sites.[1d,1e] In a few cases organic ferromagnets lacking metal ions have been prepared.[1g,1i] The magnetic ordering temperatures T_c can range up to 400 K for active-organic magnets containing metal-ion-based spins, but only up to 1.48 K for metal-ion-free systems.[1d,1e] Active ligands are rare and have been limited to strong electron acceptors, e.g. cyanocarbons [tetracyanoethylene (TCNE)],[1a–1e] chloranil,[2] and nitronyl nitroxides.[1f,1j,3] [Mn(porphyrin)][TCNE] (TCNE = tetracyanoethylene) form a family of organic-based ferrimagnets with magnetic ordering temperatures as high as 28 K.[1a,4] Several related ferrimagnets based on the antiferromagnetic coupling of S = 5/2 $Mn^{II}(hfac)_2$ (Hhfac = hexafluoroacetylacetone) and S = 1/2 nitroxides,[1f,1j] as well as S = 5/2 Mn^{II} and S = 1/2 Cu^{II} sites have been reported.[3] To date systematic approaches aimed at understanding and subsequently controlling the magnetic behavior of this class of 1-D coordination polymers has primarily focused on making the TCNE electron-transfer salts of substituted manganese(II) porphyrins.[1a,4,5] These ongoing studies have identified a correlation between a decrease of the $MnNC_{TCNE}$ angle and an increase in the intrachain magnetic coupling.[5a,6] This is attributed to increasing the magnetic coupling by increasing the σ overlap of the d_z2 and π* orbitals.[6] More recently, we have sought to alter the radical anionic bridging ligand from $[TCNE]^-$ to identify its effect on magnetic behavior. This had led to the observation that the chloranil radical anion can also stabilize magnetic ordering for this class of organic magnets.[2] Replacement of TCNE with TCNQ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane) is an obvious approach, but, to date, structurally characterized materials have been elusive.[7] An exception is the reaction of TCNQ with *meso*-tetrakis(2,4,6-trimethylphenyl)porphyrinatomanganese(II), which unexpectedly forms the diamagnetic μ_4-σ-$[TCNQ]_2^{2-}$ linkage, **2**.[8] In addition to TCNQ, we identified perfluoro-TCNQ, $TCNQF_4$, as a potential acceptor to stabilize magnetic ordering for this class of magnets.

[a] Department of Chemistry, 315 S. 1400 E. RM Dock, University of Utah,
Salt Lake City, UT 84112–0850, USA
Fax: (internat.) + 1-801/581-8433
E-mail: jsmiller@chemistry.utah.edu

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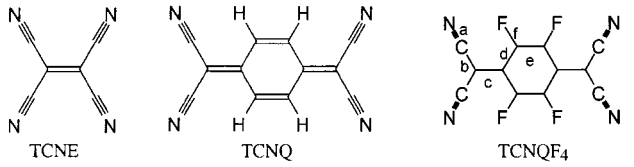

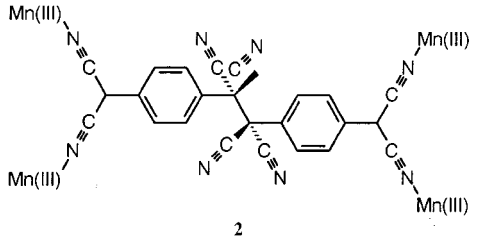

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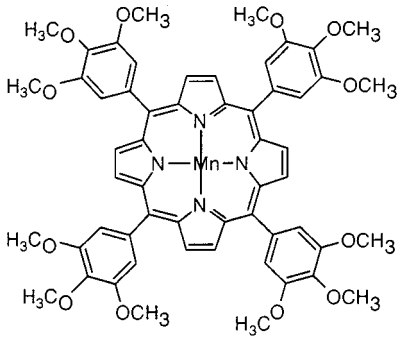
$TCNQF_4$[9] is a very strong acceptor[10] that was sought as a component in molecule-based conductors.[10b,11] Although easily reduced to form stable $[TCNQF_4]^-$ in solution, in contrast to $[TCNQ]^-$, these solids always possessed strong diamagnetic $[TCNQF_4]_2^{2-}$ dimers which did not support the formation of segregated 1-D conducting chains. Likewise, replacement of TCNE with $TCNQF_4$ to stabilize ferromagnetic ordering for the $[Fe^{III}(C_5Me_5)_2]^+[TCNE]^-$ ferromagnet, led to the formation of diamagnetic $[TCNQF_4]_2^{2-}$ dimers that did not stabilize magnetic ordering.[12] $[TCNQF_4]^-$ could form the diamagnetic μ_4-σ-$[TCNQF_4]_2^{2-}$ linkage analogous to **2**; hence the larger substituted manganese(II) porphyrin, *meso*-tetrakis(2,4,6-trimethoxyphenyl)-porphyrinatomanganese(II), $Mn^{II}T(MeO)_3PP$ **(1)**, and herein we report the synthesis, structure and bulk magnetic properties of $[Mn^{III}T(MeO)_3PP][TCNQF_4]\cdot xC_6H_4Cl_2$, $\mathbf{1}\cdot xC_6H_4Cl_2$.



$Mn^{II}T(MeO)_3PP$

Results and Discussion

The reaction of $TCNQF_4$ and $Mn^{II}T(MeO)_3PPpy$ in 1,2-$C_6H_4Cl_2$ forms $[Mn^{III}T(MeO)_3PP][TCNQF_4]\cdot 3C_6H_4Cl_2$, $\mathbf{1}\cdot 3C_6H_4Cl_2$. The ν_{CN} IR absorptions at 2196 (m) and 2165 (s) cm^{-1} are too low in energy for $TCNQF_4$ [i.e. 2225 cm^{-1}],[12,13] and too high in energy for $[TCNQF_4]^{2-}$ [i.e. 2168 (s) and 2133 (s) cm^{-1}].[12] These values are comparable to 2195 ± 1 (s) and 2177 ± 2 (s) characteristic of $[TCNQF_4]_2^{2-}$,[12,13] but the lower value is sufficiently different to suggest a different bonding mode for $[TCNQF_4]^-$.

The solvent content of the sample used for magnetic measurements was determined to be 2.3 solvent molecules per formula unit by TGA heating at a rate of 15 °C/min starting from 38 °C. Weight loss was observed immediately and all three solvent molecules were lost by 130 °C, after which decomposition was observed as a steady weight loss to 400 °C. The mass spectra showed the effluent of the TGA contains only solvent. Other solvents were also tried, but only *o*-$C_6H_4Cl_2$ gave an identical IR spectrum to the magnetic material.

X-ray Crystal Structure

$\mathbf{1}\cdot 3C_6H_4Cl_2$ (Figure 1) is composed of alternating chains of $[MnTPP]^+$ cations and $[TCNQF_4]^-$ anions. The three 1,2-dichlorobenzene solvent molecules fill the voids of the structure and are the only source of disorder. This disorder is observed in the 1,2-$C_6H_4Cl_2$ which occupies two positions that are related by a C_2 symmetry operation.

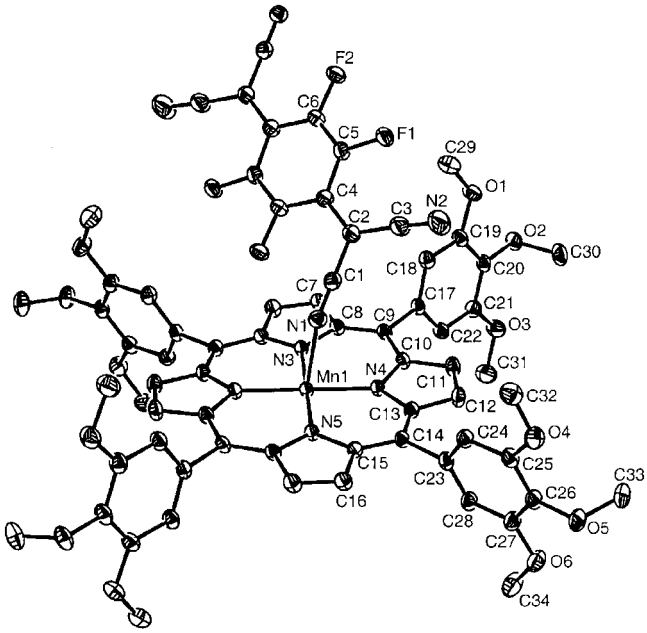
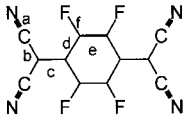


Figure 1. ORTEP drawing (50% probability level) and atom labeling diagram; the three solvent molecules are omitted for clarity

The $[MnT(MeO)_3PP]^+$ cations lie on crystallographic inversion centers with Mn at the center. The Mn^{III} atoms lie at the inversion center with $Mn–N_{por}$ distances averaging 2.004 Å, consistent with typical $[MnTPP]^+$ distances.[2,4,5a–5c,8,14] The trimethoxyphenyl-substituent plane is rotated 80° from the mean porphyrin plane.

The $TCNQF_4$ is essentially planar with a small deviation of the dicyanomethylene moiety which is twisted from the benzenoid ring plane by 5°. The $C_F–C_F$, $C_F–C_C$, and $C_C–C_{CN}$ distances are 1.352(4), 1.410(4), and 1.410(4) Å, respectively, which differ from $TCNQF_4^0$ by 0.02, 0.03, and 0.04 Å, respectively,[10b,12,15] but are comparable to the values for reduced $TCNQF_4$ as $[TCNQF_4]_2^{2-}$.[10,13,16] The bond lengths for $\mathbf{1}\cdot 3C_6H_4Cl_2$ are summarized along with other reported structures for $[TCNQF_4]^n$, Table 1. The key bond length that best describes the oxidation state of the $TCNQF_4$ is the distance *c*. This quinone-type bond in-

Table 1. Summary of the chemically different bond lengths for structurally characterized $[TCNQF_4]^n$ (n = 0, 1–, 2–)



Distances[a] in $[TCNQF_4]^n$ (n = 0, 1–, 2–)	a (Å)	b (Å)	c (Å)	d (Å)	e (Å)	f (Å)	ref.
n = 0							
$TCNQF_4$	1.140	1.437	1.372	1.437	1.334	1.336	[10b]
$[Fe(C_5H_5)_2]_2[TCNQF_4]_3$	1.149	1.439	1.373	1.438	1.331	1.334	[12]
$[NMe_4][TCNQF_4]\cdot 0.5TCNQF_4$	1.15	1.46	1.35	1.43	1.32	1.33	[15b]
$[benzotrithiphene]_2[TCNQF_4]$	1.144	1.410	1.369	1.429	1.339	1.328	[15e]
[*N*-(2-OHNp)pyreneamine][$TCNQF_4$]	1.144	1.437	1.378	1.439	1.342	1.335	[15f]
$[Dithianthrene(OEt)_4][TCNQF_4]$	1.141	1.431	1.385	1.436	1.339	1.337	[15g]
[DMQtT][$TCNQF_4$]	1.138	1.423	1.380	1.440	1.339	1.327	[15c]
n = 1–							
$[Mn^{III}T(MeO)_3PP][TCNQF_4]$	1.142	1.414	1.410	1.410	1.352	1.348	[f]
[MePhen][$TCNQF_4$][b]	1.140	1.423	1.410	1.413	1.346	1.348	[16l]
[Tempo][$TCNQF_4$][b]	1.139	1.428	1.403	1.419	1.338	1.352	[16h]
[Bis(benzo)TTF][$TCNQF_4$][b]	1.143	1.424	1.411	1.415	1.351	1.352	[16i]
$[(CH_2)_6TSeF][TCNQF_4]$[b]	1.142	1.430	1.405	1.413	1.360	1.349	[16j]
[TTF][$TCNQF_4$][b,g]	1.171	1.539	1.332	1.439	1.318	1.283	[16k]
$[Fe(C_5H_5)_2]_2[TCNQF_4]_3$[b]	1.148	1.423	1.418	1.418	1.345	1.364	[12]
$[Fe(C_5H_5)_2]_2]$ $[TCNQF_4]$[b]	1.140	1.435	1.429	1.420	1.360	1.349	[12]
$[Me_2Phen][TCNQF_4]$[b]	1.144	1.429	1.415	1.415	1.353	1.354	[16g]
[*N*-BuPhen][$TCNQF_4$][b]	1.144	1.417	1.413	1.410	1.350	1.346	[16d]
$[Cp_2Mo_2(SMe)_4][TCNQF_4]$[c,d]	1.139	1.429	1.397	1.410	1.365	1.337	[16f]
$[W(n\text{-}C_5H_4Bu t)_2(C_3S_5)][TCNQF_4]$[d]	1.145	1.423	1.393	1.421	1.340	1.331	[15d]
$[Cp_2Modmid][TCNQF_4]$[d]	1.146	1.418	1.425	1.412	1.362	1.338	[16e]
$[Cp_2Wdmid][TCNQF_4]$[d]	1.15	1.42	1.42	1.423	1.362	1.333	[16e]
$[Cp_2Modmit][TCNQF_4]$[d]	1.14	1.42	1.44	1.40	1.37	1.35	[16e]
$[Cp_2Wdmit][TCNQF_4]$[d]	1.14	1.42	1.414	1.420	1.358	1.341	[16e]
$[Cp_2Modsit][TCNQF_4]$[d]	1.15	1.43	1.42	1.43	1.33	1.35	[16e]
$[Cp_2Wdsit][TCNQF_4]$[d]	1.14	1.43	1.42	1.41	1.37	1.34	[16e]
$[Fe(C_5Me_5)_2][TCNQF_4]$[b]	1.149	1.425	1.418	1.412	1.356	1.347	[12]
$[NMe_4][TCNQF_4]\bullet 0.5TCNQF_4$[b]	1.135	1.142	1.42	1.40	1.35	1.35	[15b]
n = 2–							
$[Fe(C_5H_5)_2]_2[TCNQF_4]$	1.154	1.403	1.457	1.398	1.373	1.359	[16a]

[a] Distances are averaged if more than one was reported. – [b] $[TCNQF_4]_2^{2-}$ – [c] $TCNQF_4$'s in dimer are offset by ca. 45°; diamagnetic. – [d] $[\sigma\text{-}TCNQF_4]_2^{2-}$. – [f] This work. – [g] Not plotted in Figure 2 as the unusual deviation of the reported bond length with respect to the other compounds in this table.

creases as the negative charge increases for $[TCNQF_4]^n$. This increase in negative charge is also evidenced by the contraction of bond d and a lengthening of bond e. When the bond length for c is plotted for each of the compounds (Figure 2) the separations of the 0, 1– and 2– species can easily be distinguished, and **1**·$3C_6H_4Cl_2$ clearly lies in the 1– regime.

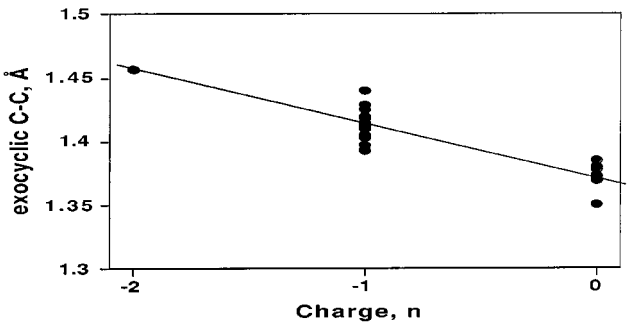


Figure 2. Bond length correlations with bond c (see Table 2) in various $[TCNQF_4]^n$ (n = 0, 1–, 2–)

This semi-quinoid-type character also causes the ring *ipso* angles to differ from the ideal 120° to 123° about F and 113° about $C(CN)_2$. The internal F angle is 118° and the external F angle is 119°. The internal C1–C2–C3 angle in 113°, while the C1–C2–C4 and C3–C2–C4 angles are 123° and 124°, respectively. Hence, in accord with the IR data (vide supra) $[TCNQF_4]^-$ must be present. $[TCNQF_4]^-$ is *trans*-μ bonded to two Mn^{III} atoms with a distance of 2.321(3) Å and an $MnNC_{TCNF4}$ angle of 135.9(2)°. The MnN_{TCNF4} distance is in the range noted for $[TCNE]^-$ analogs;[2,4,5a–5c,8,14] however, this angle is smaller than that observed for [Mn(porphyrin)][TCNE] systems, namely, the MnNC angle which range from 140° to 165°. This is presumably due to the additional space to be filled from the larger acceptor. The dihedral angle between the mean MnN_4 and the mean $[TCNQF_4]^-$ planes is 46.4°. This is in the range of those observed for the [Mn(porphyrin)][TCNE] class of compounds that range from ca. 33.4 to 89.4°.[2,4,5a–5c,8,14] The intrachain Mn···Mn separation is 12.685 Å, which, as expected due to the larger length of $[TCNQF_4]^-$ with respect to $[TCNE]^-$, exceeds the range of

intrachain Mn···Mn separations (i.e. 8.587 to 10.376 Å).[2,4,5a–5c,8,14] The interchain Mn···Mn separations of 16.959, 18.759, and 23.663 Å are also larger than those observed for the $[TCNE]^-$ electron transfer salts which is attributed to the larger spin-bearing ligand used; this is also consistent with the [Mn^{III}TPP][chloranil] magnet.[2]

In the solid state **1**·$3C_6H_4Cl_2$ forms parallel 1-D chains comprised of alternating S = 2 cations and S = 1/2 anions. All chains are identical and possess a zigzag motif (Figure 3). This is a result of the $TCNQF_4$'s aligning *cis* with respect to each other about the manganese center. These uniform chains are arranged into offset layers giving rise to two different interchain Mn···Mn distances as depicted in Figure 3. This zigzag motif is observed for the first time for this $[Mn(porphyrin)]^+$ family of magnets; however, the effect of the structural arrangement on the magnetic properties is uncertain at present.

Magnetic Behavior

The magnetic susceptibility, χ, of **1**·$2.3C_6H_4Cl_2$ in the range 2 to 300 K can be fit to the Curie-Weiss expression, $\chi \propto 1/(T - \theta)$, with $\theta = -37$ K ($T > 250$ K), and an effective θ',[5b] of 29 K ($75 < T < 200$ K), Figure 4.

This θ'-value is markedly lower than the values observed in [Mn(porphyrin)][TCNE] uniform chain systems which range from 42 to >200 K.[1a,5] The room temperature effective moment, μ_{eff} [$\equiv(8\chi T)^{1/2}$], value is 4.81 μ_B which is slightly lower than the predicted value of 5.20 μ_B for an uncoupled S = 1/2, S = 2 system. The $\chi T(T)$ plot have a minimum at 215 ± 10 K (see Figure 4) characteristic of ferrimagnetically coupled systems.[17] The position of this minimum is responsible for the observed lower room temperature χT values. With decreasing temperature $\chi T(T)$ reaches a maximum at 9 K with a value of 10.2 emuK/mol, due to saturation, and then decreases rapidly. The $\chi T(T)$

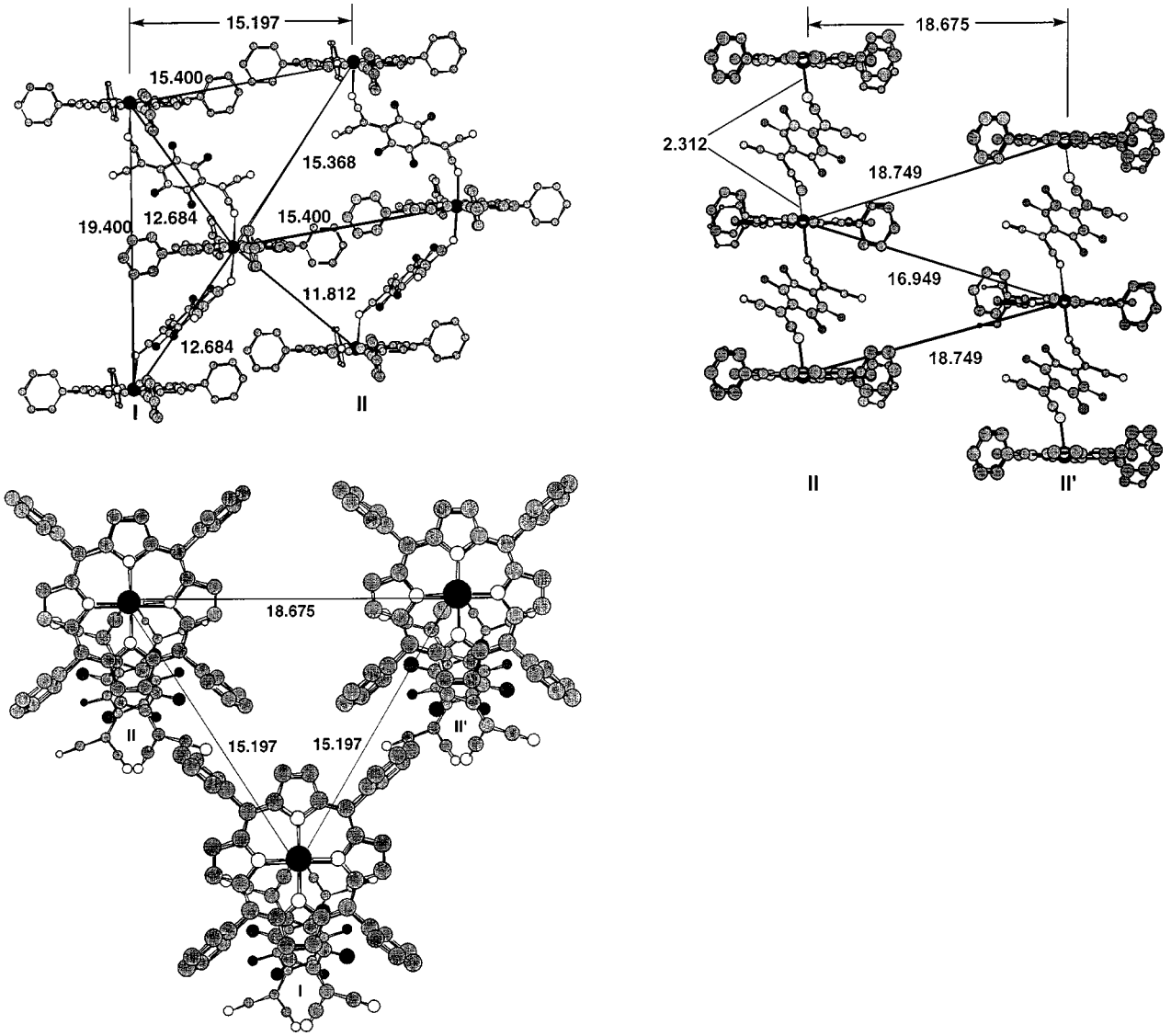


Figure 3. Views of intra- and interchain interactions among the unique chains: **I**, **II**, and **III** for [$MnT(MeO)_3PP$]-[$TCNQF_4$]·$3C_6H_4Cl_2$

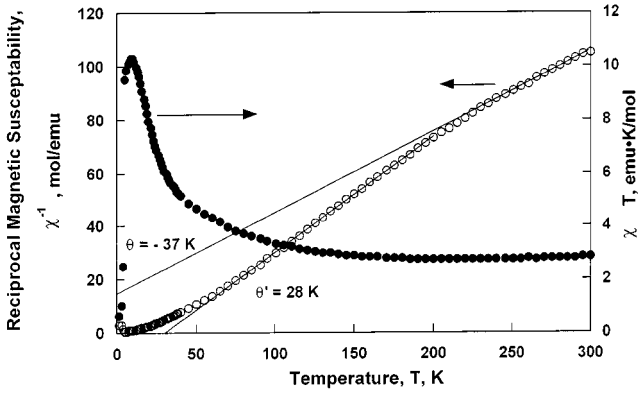


Figure 4. $\chi^{-1}(T)$ (o), and the $\chi T(T)$ (•) fit to the Seiden model (solid line) with $J/k_B = -71$ K (49 cm^{-1}) for $H = -2J\boldsymbol{S}_i\cdot\boldsymbol{S}_j$.for polycrystalline **1**·2.3$C_6H_4Cl_2$; the sample was cooled to 2 K in zero field, then the field (1000 Oe) was turned on and data was measured whilst warming to 300 K

data above 150 K can be fit to the Seiden model[18] for non-interacting chains comprised of alternating $g = 2$ quantum $S = 2$ and classical $S = 1/2$ spins, with $J/k_B = -71$ K (–49 cm^{-1}; –61 meV) for $H = -2J\mathbf{S}_i\cdot\mathbf{S}_j$, Figure 4. The deviation below 150 K is attributed to the onset of three-dimensional interactions and exceeds the values predicted by the model. Below 47 K, however, the slope of the calculated $\chi T(T)$ data begins to rise faster than the experimental data. This type of crossover has not been observed before in this family of magnets, but may be attributed to short correlation lengths. These short correlation lengths are also manifested in the lowered maximum of the $\chi T(T)$ data.

Antiferromagnetic behavior is also evident from the saturation magnetization. The isothermal magnetization at 2 K increases rapidly with the application of a small field, quickly rising to near saturation, M_s (see Figure 5). At 2 T the magnetization is 14.900 emuOe/mol or 89% of 16.755 emuOe/mol expected for an $S_{Tot} = 2 - 1/2 = 3/2$ system. This is substantially lower than that expected from ferromagnetic coupling, i.e. 27.925 emuOe/mol for an $S_{Tot} = 2 + 1/2 = 5/2$ system. At 2 K metamagnetic behavior is observed (field-induced changeover from an antiferromagnetic ground state to a ferromagnetic ground state) with a critical field of ca. 20.2 kOe, Figure 5. Similar field-dependent behavior was observed for [MnTPP][TCNE], which exhibits a

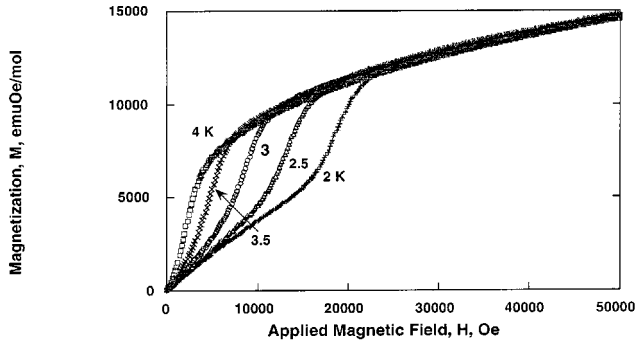


Figure 5. The magnetization curves taken at 2, 2.5, 3, 3.5, and 4 K for **1**·2.3$C_6H_4Cl_2$ displaying the disappearance of the metamagnetic behavior as the temperature is increased; the inset displays a critical field of 20.2 kOe taken from the 2 K saturation data.(solid line)

critical field of ca. 30 kOe at 2.25 K corresponding to a spin-flop transition.[19]

The field-induced crossover from an antiferromagnetic ground state to a ferromagnetic ground state is not observed above 4 K. Sample-independent hysteresis with a large coercive field of 17.1 kOe is observed at 2 K (Figure 6), but is not observed at 5 K. The 2 K remnant magnetization is 7.200 emuOe/mol. The field-cooled and zero-field-cooled data $M(T)$ data at 0.1, 1, and 10 Oe, show a bifurcation at 5.4 K (Figure 7); however, this is not a good measure of T_c since the bifurcation can begin at higher temperatures and not be observable with so few data points.

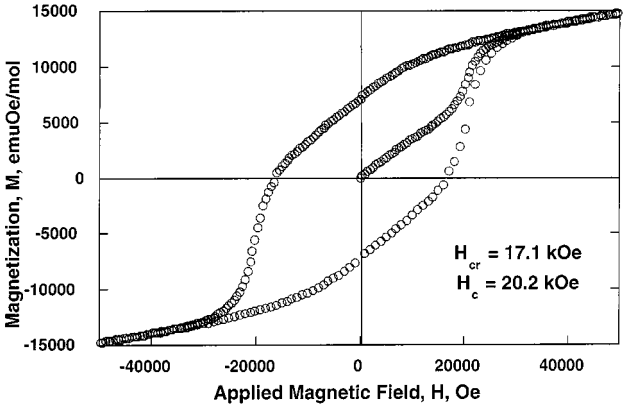


Figure 6. The observed hysteresis for **1**·2.3$C_6H_4Cl_2$ taken at 2 K; the sample was frozen in mineral oil and cooled in zero applied field

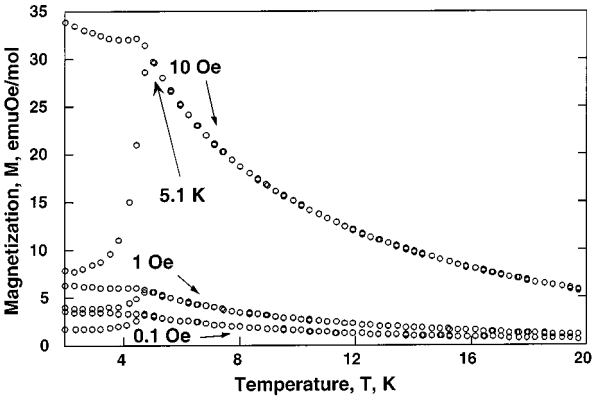


Figure 7. The field cooled and zero-field-cooled data for **1**·2.3$C_6H_4Cl_2$ displaying bifurcation at fields of 0.1, 1.0, and 10 Oe

In addition to dc measurements, the susceptibility was determined in an applied ac field of 1000 Oe (<0.05 dc field) at several frequencies and the resulting data are consistent with long-range ferromagnetic order. A peak in the real part of the 10 Hz ac susceptibility $\chi'(T)$ at 7.3 K is a better measure of T_c (Figure 8). An out-of-phase component, $\chi''(T)$, characteristic of a noncompensated moment is present with a peak at 6.3 K. There are also large frequency dependencies of both $\chi'(T)$ and $\chi''(T)$. The frequency dependence of $\chi'(T)$, ϕ [$= (T_{1000\ Hz} - T_{10\ Hz})/\{T_{10\ Hz}[\log(1000/10)]\}$], is 0.17 which is characteristic of the material being a

spin glass or superparamagnetic state.[20] The broad nature of the $\chi'(T)$ and $\chi''(T)$ peaks suggests that more than one transition is occurring.

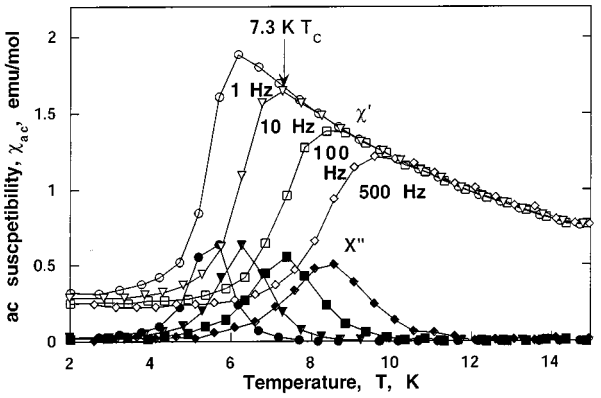


Figure 8. The dispersive, χ', and absorptive, χ'', components of the a.c. susceptibility measured at 1, 10, 100 and 500 Hz for **1**·2.3$C_6H_4Cl_2$; the 7.3 K absorption in the 10 Hz frequency data is defined as T_c; the sample was cooled to 2 K in zero field and data was taken upon warming

Experimental Section

Synthesis: All manipulations were carried out in a Vacuum Atmospheres DriLab under nitrogen. All glassware was oven dried at 110 °C and immediately pumped into the DriLab. The solvents were dried from appropriate drying agents under nitrogen. 3,4,5-Trimethoxybenzaldehyde (Acros) was used as received. $H_2T(MeO)_3PP$ was synthesized by modified literature methods,[21] The $MnT(MeO)_3PPCl$ was prepared by refluxing the free base in DMF with $Mn(OAc)_2{\cdot}4H_2O$ (Acros) and shaking with brine. $Mn^{II}T(MeO)_3PPpy$ was prepared by literature methods.[22] $TCNQF_4$, a gift from O. Webster, was recrystallized prior to use.

$[Mn^{III}T(MeO)_3PP][TCNQF_4]$·x*o*-$C_6H_4Cl_2$: This compound was prepared by adding a filtered solution of $TCNQF_4$ (12 mg, 0.043 mmol) dissolved in hot 1,2-dichlorobenzene (10 mL) to a filtered solution of $Mn^{II}T(MeO)_3PPpy$ (32 mg, 0.043 mmol) in hot 1,2-dichlorobenzene (5 mL). The resulting solution was allowed to stand for three weeks, and the black crystals (11 mg) formed were collected by vacuum filtration. Identical material can be obtained by refluxing $Mn^{II}T(MeO)_3PPpy$ and $TCNQF_4$ for 10 min and letting the solution cool to room temperature. Upon addition of hexane, a black precipitate can be collected on a fritted glass disc with a yield of approximately 70%. The black filtrate was washed with hexane (2 × 5 mL), then stored under nitrogen. – IR: ν_{CN} = 2196(m) and 2165(s) cm^{-1}.

X-ray Structure Determination: Isolation of crystals suitable for X-ray diffraction is described above. The crystal, in the mother liquor, was mounted on a glass fiber covered in oil, mounted on the goniometer and rapidly cooled in a stream of liquid nitrogen at 200 K. Data was collected at 200 K with a Nonius Kappa CCD-based X-ray diffractometer system operated at 2000 W power. The cell constants and an orientation matrix for the data collection were obtained by least-squares refinement of 6707 reflections; the key crystallographic information is given in Table 2. The crystal structure was solved by direct methods using SHELXL97.[23] Non-hydrogen atoms were refined anisotropically. Only one of the three solvent molecules is disordered, which was detected through the use of difference electron maps which illustrated a second orientation of the solvent. These two orientations were fit with the aid of a graphics workstation and the model was refined. The bonds and angles for this solvent were restrained to a standard geometry throughout the refinement.

Table 2. Summary of the crystallographic data for $[MnT(MeO)_3PP][TCNQF_4]{\cdot}3C_6H_4Cl_2$

Chemical formula	$C_{86}H_{64}Cl_6F_4MnN_8O_{12}$
M_r, Dalton	1745.09
Space group	*C*2/*c*
a	16.9486(10) Å
b	25.7170(14) Å
c	19.4009(12) Å
β	107.091(4)°
V	8082.8(8) $Å^3$
Z	4
T	200 K
λ	0.71073 Å
ρ_{calcd}	1.434 $g{\cdot}cm^{-3}$
μ_{calcd}	0.439 mm^{-1}
$R(F_o)$[a]	0.0547
$R_w(F_o)$[b]	0.1340

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

Crystallographic data (excluding structure factors) for the structure reported herein have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-129223. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

Physical Methods: The magnetic susceptibility was determined as previously reported.[2] The diamagnetic correction for the 2.3 equiv. of the 1,2-$C_6H_4Cl_2$ solvate (as determined by TGA) was calculated using Pascal's constants to be -951×10^{-6} emu/mol.

The thermal properties were studied on a TA Instruments Model 2050 thermogravimetric analyzer (TGA, ambient to 1000 °C) placed in a Vacuum Atmospheres DriLab under argon, to retain the integrity of air- and water-sensitive samples. Samples were placed in an aluminum pan and heated to 450 °C at 15 °C/min under a continuous flow of nitrogen (10 mL/min).

The infrared spectra were recorded on a BioRad FTS 40 FTIR in the range of 650 to 4000 cm^{-1} on NaCl discs as a mineral oil mull.

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