Structure and magnetic properties of *meso*-tetrakis(2,4,6-trimethylphenyl)porphyrinatomanganese(III) 7,7,8,8-tetracyano-2,5-dimethyl-*p*-quinodimethanide with a 2.3 K T_c. The first example of *cis* coordination of a tetracyano-*p*-quinodimethanide

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The crystal structure of *meso*-tetrakis(2,4,6-trimethylphenyl)porphyrinatomanganese(III) 7,7,8,8-tetracyano-2,5-dimethyl-*p*-quinodimethanide, [MnTMesP][DMTCNQ]·2*p*-C$_6$H$_4$Me$_2$ provides the first example of a *cis*-1,2-μ-coordination motif having an infinite zigzag chain structure. [MnTMesP][DMTCNQ]·2*p*-C$_6$H$_4$Me$_2$ crystallizes in a triclinic $P\bar{1}$ space group. The zigzag one-dimensional (1-D) chain is non-uniform and each acceptor does not lie on a centre of symmetry, although all acceptors are crystallographically equivalent. The ionic ground state of the complex was determined on the basis of X-ray photoelectron spectroscopy, crystallographic data, as well as the ν_{CN} at 2184 and 2160 cm^{-1}. The susceptibility (χ) of the complex obeys the Curie–Weiss equation, $\chi = 1/(T-\theta)$, where θ is -10 ± 1 K ($130 < T < 250$ K), and $+23 \pm 1$ K ($T > 250$ K). A minimum of $\chi T(T)$ characteristic of 1-D antiferromagnetic coupling is observed at 115 K. Above 50 K, $\chi T(T)$ can be fitted by the Seiden model for non-interacting chains comprised of alternating $g = 2$, quantum $S = 2$ and classical $S = 1/2$ spins, with $J/k_B = -39$ K for $H = -2JS_i \cdot S_j$. The in-phase component, $\chi'(T)$, in a.c. susceptibility measurements shows a sharp maximum at 2.3 K associated with the ordering temperature, T_c, of the material.

Introduction

In the past two decades[1] magnetically ordered molecular materials have attracted much attention for attaining a high degree of coupling among unpaired electron spins. Molecular magnets based on electron transfer salts (ETS) which are comprised of organic cation and organic anion radicals have a unique position in this field of this research, since electrostatic attractive forces lead to strong intermolecular interactions in the solid state and the subsequent short intermolecular contact results in a strong exchange interaction. The magnetic ordering temperatures, T_c, qualitatively reflect these interactions. For example, the 8.8 K T_c observed for ionic [MnCp*$_2$][TCNE][2] is about six times higher than that for a magnet constructed by simple van der Waals interactions such as a nitronyl aminoxyl derivative with a 1.48 K T_c.[1e] Furthermore, the ETS with an organic anion radical bonded to a paramagnetic transition metal cation have stronger exchange interactions *via* covalent bonding and enhanced T_c. The system with the highest T_c, V(TCNE)$_x$·yCH$_2$Cl$_2$ ($x \approx 2$; $y \approx 1/2$), has the largest number of bonds between the [TCNE]$^{\cdot-}$ and paramagnetic transition metal. Unfortunately the amorphous nature of this room temperature magnet prevents the detailed understanding of the structure.

The ETS based on prophyrinatomanganese ([MnP]) with cyanocarbon acceptors such as TCNE are frequently structurally well characterized with magnetic ordering temperatures as high as 28 K.[3–6] These [MnP][TCNE] complexes possess a one-dimensional (1-D) polymeric structure where the [MnP]$^+$ cations are bridged in a *trans*-μ fashion between Mn^{III} and

nitrile groups of [TCNE]$^{\cdot-}$. Further studies on [MnP][TCNE] are needed to obtain new magnets with enhanced physical properties such as a higher T_c and a stronger coercive force, H_{cr}. We have focused on the following two strategies. One is to establish a relationship between the angle of the MnNC^{TCNE} and the magnitude of the intrachain magnetic coupling.[7] This is related to the hypothesis that the intrachain magnetic coupling increases with an increase in the σ overlap between the Mn^{III} d$_{z^2}$ and [TCNE]$^{\cdot-}$ π* orbitals.

The second strategy is to find more suitable open shelled bridging ligands than [TCNE]$^{\cdot-}$. For this purpose we have examined acceptor molecules such as hexacyanobutadiene[8–10] and chloranil.[11] These led to the conclusion that radical anions, having larger π-electron systems than [TCNE]$^{\cdot-}$, can also stabilize magnetic ordering for this class of organic magnets. To obtain deeper understanding of these magnets, new acceptors that can stabilize ferrimagnetic ordering are sought. Several groups have replaced TCNE with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ). However, no information concerning on the structure of these complexes was available.[6,12] Recently, we reported the unprecedented honeycomb supramolecular structure as a product of TCNQ and *meso*-tetrakis(2,4,6-trimethylphenyl)porphyrinatomanganese-(II) (Mn^{II}TMesP).[13] However, the diamagnetic dimerized dianion of TCNQ, σ-[TCNQ]$_2^{2-}$ **1**, did not stabilize magnetic ordering. Two methyl groups were introduced into TCNQ to give 7,7,8,8-tetracyano-2,5-dimethyl-*p*-quinodimethane (DMTCNQ), with the goal of stabilizing a magnet. Herein, we report the first isolation and characterization of an ETS of DMTCNQ with Mn^{II}TMesP having a novel *cis* coordination.[14,15]
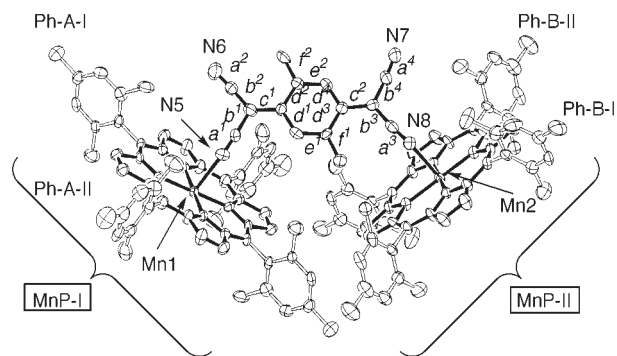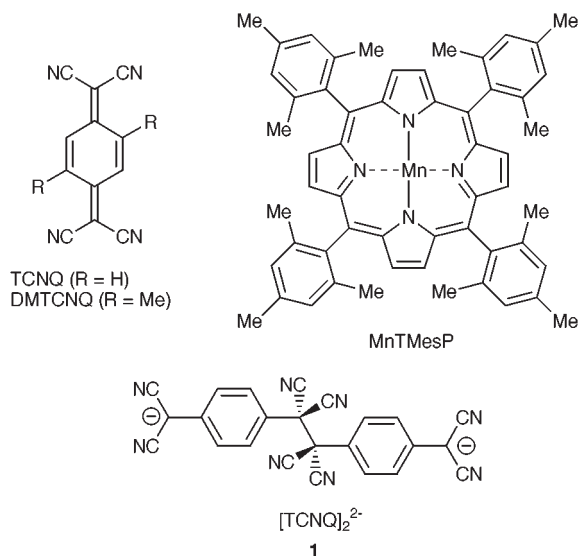
Fig. 1 Atom labelling ORTEP[20] drawing of [MnTMesP]-[DMTCNQ]·2p-C$_6$H$_4$Me$_2$. Thermal ellipsoids are the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. The crystallographically unique atoms are labeled. The dihedral angles of mesityl groups to porphyrin planes are as follows: Ph-A-I, 76.0; Ph-A-II, 82.0; Ph-B-I, 89.3; Ph-B-II, 81.1°. Intramolecular bond distances a–f of [DMTCNQ]$^-$ are given in Table 1.

Results and discussion

Synthesis

The reaction of [Mn^{II}TMesP]·C$_5$H$_5$N[13] with DMTCNQ in p-xylene led to the isolation of [MnTMesP][DMTCNQ]·2p-C$_6$H$_4$Me$_2$. This ETS is a *porphyrin sponge*[16] as it incorporates two solvent molecules, p-xylene in this case. In contrast to other [MnP][TCNE],[4] the present crystal includes exactly two solvent molecules even after vacuum drying at room temperature, suggesting relatively strong solvent binding at that temperature. Interestingly, thermogravimetric analysis (TGA) showed both solvent molecules were lost below 158 °C, after which decomposition was observed as a steady weight loss to 220 °C.

It is well known that the nitrile stretching mode (ν_{CN}) of TCNQ is a sensitive marker for its ionization state, *i.e.* the value decreases with increase of negative charge.[17] The values of [MnTMesP][DMTCNQ] (2184 and 2160 cm^{-1}) are shifted from the 2223 and 2212 cm^{-1} observed for neutral DMTCNQ^0 and those for the reported partial ETS of [DMTCNQ]$^{0.5-}$ (2214–2190 cm^{-1}).[18] The value is comparable to that for the potassium complex (2184 cm^{-1})[19] and ionic 2,3-DMTSA complex (2172 cm^{-1}),[2,18] which is consistent with reduction of DMTCNQ to [DMTCNQ]$^-$.

Structure

Single crystal X-ray analysis revealed that [Mn^{III}T-MesP][DMTCNQ]·2p-C$_6$H$_4$Me$_2$ forms 1-D chains comprised of alternating [Mn^{III}TMesP]$^+$ and [DMTCNQ]$^-$ where each Mn^{III} is six-coordinated to two [DMTCNQ]$^-$ in a trans-μ-N-bound manner (Figs. 1 and 2). The Mn are cis bound to the [DMTCNQ]$^-$, the first report of this novel coordination pattern for TCNQs.[21,22] This is in marked contrast to the known 1-D coordination polymeric motif, albeit trans, observed for most magnetically ordered [MnP][TCNE] complexes.[4]

The structure contains two crystallographically independent porphyrin molecules, MnP-I and MnP-II, with similar gross conformations (Fig. 1). The dihedral angles between the porphyrin plane and the aryl groups are 76.0 and 82.0° for MnP-I, and 89.3 and 81.1° for MnP-II. These values are comparable to those of H$_2$TMesP (83.6°).[23] The dihedral angles between [DMTCNQ]$^-$ and MnP-I or MnP-II are 56.8° or 49.0°. Interestingly, these angles are in the range of those observed for [MnTPP][TCNE] (*ca.* 33–89°),[4,7] although the steric repulsion between the mesityl groups and [DMTCNQ]$^-$ is as expected.

The [DMTCNQ]$^-$ bond lengths differ significantly from those for neutral DMTCNQ^0 complexes (Table 1)[18,19,24–26] and neutral TCNQ^0. The key bond distances that best describe the oxidation state of the TCNQs are the *exo*-methylene c^1 and c^2. These distances are 1.43(1) and 1.45(1) Å both of which are more than 0.06 Å longer than those for DMTCNQ which range from 1.347 to 1.398 Å. These quinone-type bonds become longer with an increase of negative charge in TCNQs. The increase in negative charge also results in the contraction of d^1–d^4 and a lengthening of e^1 and e^2. These changes are attributable to the aromatic character of the central six-membered ring after electron transfer. Reflecting the single bond character of c^1 and c^2, the [DMTCNQ]$^-$ in the complex is non-planar, with the dicyanomethylene units rotated toward the central six-membered ring around these bonds. This is in marked contrast to the planar structure of neutral DMTCNQ.[25] Hence, in accord with the IR ν_{CN} and the XPS (*vide infra*) data, [DMTCNQ]$^-$ is present in this complex.

The N5 and N8 atoms of [DMTCNQ]$^-$ are cis bound to manganese and produce a 1-D zigzag chain comprising alternating $S = 2$ cations and $S = 1/2$ anions (Fig. 2). Several different coordination motifs of TCNQ, *i.e.* mono ($\eta^1$$^-$), 1,1, trans-1,2-μ, μ$_3$, and μ$_4$, have been reported.[21] This cis-1,2-μ-motif was observed for the first time. The dihedral angle between the two adjacent porphyrin rings in the chain is 109.7°, which is the largest value among those for reported 1-D [MnP] complexes,[27] but different from the parallel alignment of usual uniform [MnP][TCNE].[4] Only Mn1 and Mn2 are located on an inversion centre. As observed for the low temperature phase of [MnTF$_4$OMePP][TCNE],[2,28] the acceptor molecule lacks symmetry elements, *i.e.*, the 1-D chain is non-uniform. The Mn–N^{DMTCNQ} distances are 2.345(9) and 2.318(9) Å and MnNC^{DMTCNQ} angles are 141.9(9) and 142.5(9)° for MnP-I and MnP-II, respectively, and hence are chemically equivalent. Both the MnN^{DMTCNQ} distances and MnNC^{DMTCNQ} angles are in the range observed for [MnP][TCNE].[4,7] The intrachain Mn···Mn separation is 11.43 Å, which, as expected due to the larger length of [DMTCNQ]$^-$ than [TCNE]$^-$, exceeds the range of intrachain Mn···Mn separations (8.587 to 10.376 Å) of [MnP][TCNE].[4,7]

The 1-D non-uniform zigzag chain interacts with the nearest chain in an out-of-registry manner (Fig. 3). The interchain Mn···Mn separations are 15.66, 16.78, and 21.68 Å are also larger than those observed for the [TCNE]$^-$ ETS which is attributed to the larger spin-bearing ligand. This is also consistent with other magnets of hexacyanobutadiene[8] and chloranil.[11]
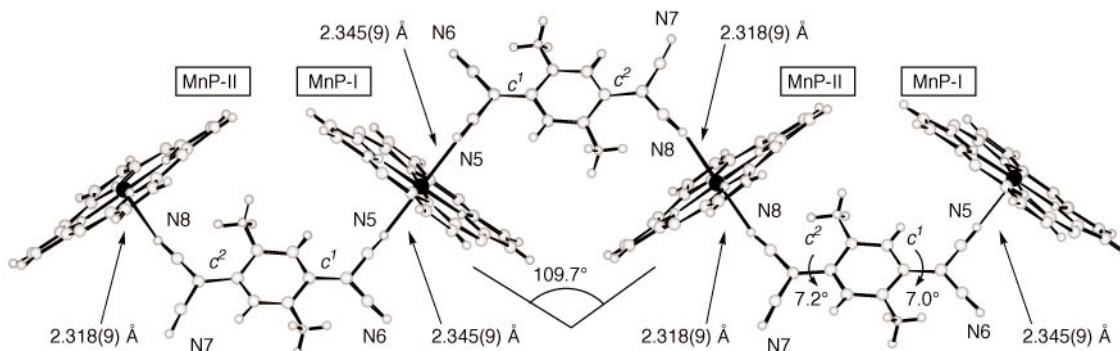
Fig. 2 A segment of the 1-D chain structure. For clarity, solvent molecules and mesityl groups of [MnTMesP]$^+$ are omitted. Only Mn^{III} is located on the inversion center of $P\bar{1}$ space group.

X-Ray photoelectron spectroscopy

X-Ray photoelectron spectroscopy (XPS) provides direct information about the electronic structure of the complexes in MnTPPs (Table 2). The Mn core ionization potentials were observed at 642.8 eV and 654.6 eV for Mn2p$_{3/2}$ and Mn2p$_{1/2}$, respectively. These values are larger than those for Mn^{II} (641.1 and 653.1 eV).[29] Furthermore, the values are much closer to those of six-coordinated [Mn^{III}TPP][TCNE]·2C$_6$H$_5$Me (642.6 and 654.2 eV) than five-coordinated [Mn^{III}TPP]Cl (642.2 and 653.8 eV), suggesting that Mn^{III} in [Mn^{III}TMesP][DMTCNQ] is six-coordinated as structurally observed. The IR and the XPS data as well as the observed bond lengths of DMTCNQ (*vide infra*) support electron transfer from Mn^{II} to DMTCNQ yielding $S=2$ for [Mn^{III}TMesP]$^+$ and $S=1/2$ for [DMTCNQ]$^{.-}$.

Magnetic behaviour

The magnetic susceptibility (χ) was measured between 2 and 300 K and could be fitted by the Curie–Weiss equation, $\chi=1/(T-\theta)$, with θ of -10 ± 1 K ($130<T<250$ K), and an effective θ, θ', of $+23\pm1$ K ($T>250$ K) (Fig. 4). The θ' value is markedly smaller than the values observed for [MnP][TCNE] uniform chain systems which range from 12 to >100 K.[4–6] The 300 K effective moment is 5.10 μ_B (Fig. 5) in good agreement with the expected values for independent isotropic values of $g=2$, $S=2$ for Mn^{III} and $S=1/2$ of [DMTCNQ]$^{.-}$ (5.20 μ_B). A minimum in the $\chi T(T)$ plot characteristic of 1-D antiferromagnetic coupling[30] is observed at 115 K (Fig. 4). The minimum is responsible for the observed lower room temperature χT and effective moment. With decreasing temperature $\chi T(T)$ reaches a maximum at 10 K with 115 emu K mol^{-1} due to saturation and then decreases rapidly.

Above 50 K, $\chi T(T)$ can be fitted by the Seiden model[31] for non-interacting chains comprised of alternating $g=2$, quantum $S=2$ and classical $S=1/2$ spins, wiht $J/k_B=-39$ K (-27 cm^{-1}; -53 cal mol^{-1}; -33 meV) for $H=-2JS_i\cdot S_j$ (Fig. 4). The deviation below 50 K is attributed to the onset of three dimensional interactions and the data exceed the predicted values based on the model. Such enhanced values of $\chi T(T)$ at

Table 1 Summary of the chemically different bond distances for structurally characterized [DMTCNQ]^n ($n\leqslant0$)
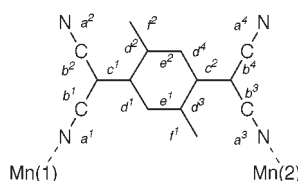
Donor	ET^a	Mn(1)–N(5)	Mn(2)–N(8)	a^1	a^2	a^3	a^4	b^1	b^2	b^3	b^4
[MnTMesP]	Full	2.345(9)	2.318(9)	1.14(1)	1.14(1)	1.17(1)	1.14(1)	1.44(1)	1.39(1)	1.41(1)	1.41(1)
2,3-DMTSA	Full			1.145(13)	1.120(11)	1.120(11)	1.145(13)	1.395(12)	1.445(11)	1.445(11)	1.395(12)
6,7-DMTSA	Partial			1.130(14)	1.155(17)	1.155(17)	1.130(14)	1.462(12)	1.443(15)	1.443(15)	1/462(12)
TMTSA	Partial			1.126(20)	1.125(17)	1.125(17)	1.126(20)	1.416(20)	1.417(8)	1.417(8)	1.416(20)
TMTTA	Partial			1.155(11)	1.132(10)	1.132(10)	1.155(11)	1.454(11)	1.428(9)	1.428(9)	1.454(11)
TMTSF	Partial			1.143(6)	1.143(6)	1.143(6)	1.143(6)	1.420(6)	1.426(6)	1.426(6)	1.420(6)
M$_2$P (296 K)	Partial			1.14(1)	1.129(8)	1.129(8)	1.14(1)	1/43(1)	1.44(1)	1.44(1)	1.43(1)
M$_2$P (162 K)	Partial			1.12(2)	1.19(2)	1.09(1)	1.21(2)	1.42(2)	1.40(2)	1.45(1)	1.45(2)
Ni(oaoH)$_2$	Neutral			1.122(8)	1.126(9)	1.126(9)	1.122(8)	1.448(8)	1.433(9)	1.433(9)	1.448(8)

|	c^1	c^2	d^1	d^2	d^3	d^4	e^1	e^2	f^1	f^2	Reference
[MnTMesP]	1.43(1)	1.45(1)	1.39(1)	1.46(1)	1.43(1)	1.40(1)	1.39(1)	1.36(1)	1.50(1)	1.49(1)	This work
2,3-DMTSA	1.438(10)	1.438(10)	1.405(10)	1.417(11)	1.417(11)	1.405(10)	1.369(11)	1.369(11)	1.547(11)	1.547(11)	18
6,7-DMTSA	1.347(12)	1.347(12)	1.462(12)	1.445(12)	1.445(12)	1.462(12)	1.357(12)	1.357(12)	1.540(12)	1.540(12)	18
TMTSA	1.388(17)	1.388(17)	1.430(17)	1.491(18)	1.491(18)	1.430(17)	1.340(17)	1.340(17)	1.529(18)	1.529(18)	18
TMTTA	1.383(8)	1.383(8)	1.435(8)	1.447(9)	1.447(9)	1.435(8)	1.340(8)	1.340(8)	1.521(10)	1.521(10)	18
TMTSF	1.398(6)	1.398(6)	1.434(6)	1.448(6)	1.448(6)	1.434(6)	1.360(6)	1.360(6)	1.506(6)	1.506(6)	24
M$_2$P (296 K)	1.39(1)	1.39(1)	1.45(1)	1.437(9)	1.437(9)	1.45(1)	1.355(9)	1.355(9)	1.489(9)	1.489(9)	19
M$_2$P (162 K)	1.41(1)	1.41(2)	1.47(1)	1.48(2)	1.42(2)	1.41(2)	1.33(1)	1.39(2)	1.55(2)	1.47(2)	19
Ni(oaoH)$_2$	1.381(8)	1.381(8)	1.436(8)	1.467(7)	1.467(7)	1.436(8)	1.346(9)	1.346(9)	1.491(8)	1.491(8)	25

^{a}Degree of charge transfer.
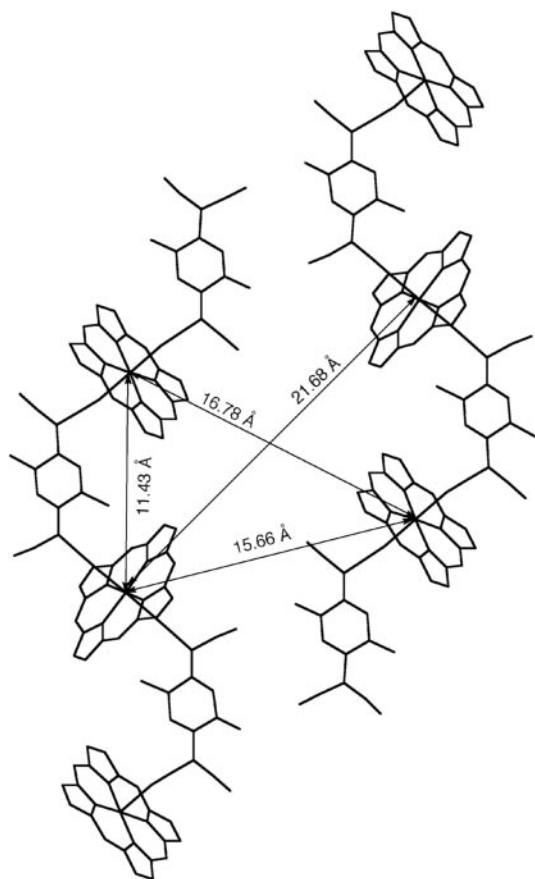
Fig. 3 The most nearest interchain out-of-registry packing interaction of the complex. For clarity, solvent molecules and mesityl groups of [MnTMesP]$^+$ are omitted. Mn···Mn interactions are indicated by arrows.
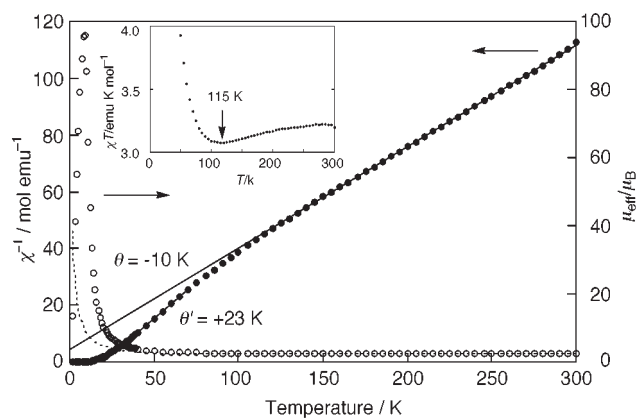

Fig. 4 $\chi^{-1}(T)$ ($\bigcirc$) and the $\chi T(T)$ ($\bullet$) fit using the Seiden model (dotted line) with $J/k_B = -39$ K (-27 cm^{-1}) for H $= -2JS_i \cdot S_j$ for polycrystalline [Mn^{III}TMesP][DMTCNQ]·2p-C$_6$H$_4$Me$_2$. The sample was cooled to 2 K in zero field, then a field of 1000 Oe was applied and the data were taken upon warming to 300 K.
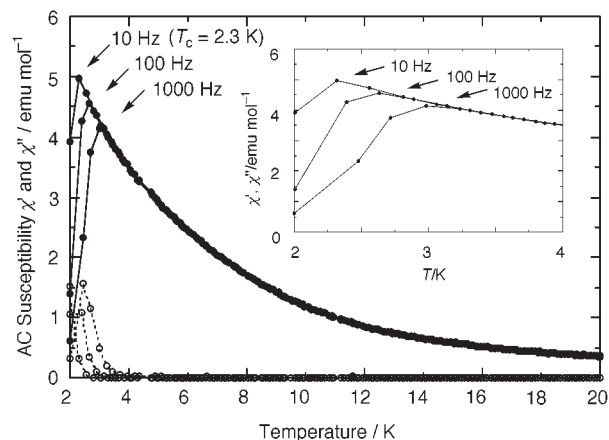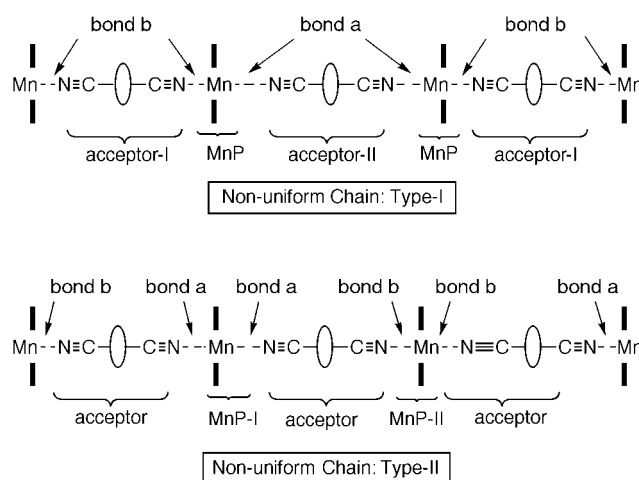

Fig. 5 The dispersive, χ' ($\bullet$), and absorptive, χ'' ($\bigcirc$), components of the a.c. susceptibility measured at 10, 100 and 1000 Hz. The 2.3 K absorption in the 10 Hz frequency data is defined as T_c. The sample was cooled to 2 K in zero field and data were taken upon warming.

low temperature with respect to those predicted from the Seiden model have been observed for other members of the [MnP][TCNE] family and attributed to ferromagnetic coupling arising from dipolar coupling.[10]

A peak in the real part of the 10 Hz a.c. susceptibility, $\chi'(T)$, at 2.3 K is a better measure of T_c, Fig. 5. An out-of-phase component, $\chi''(T)$, characteristic of an uncompensated moment, appears with a peak in the 10 Hz data that is less than 2 K. There are also large frequency dependences of both $\chi'(T)$ and $\chi''(T)$. The frequency dependence of $\chi'(T)$, $\phi[=(T_{1000\,Hz}-T_{10\,Hz})/\{T_{10\,Hz}[\log(1000/10)]\}]$, is 0.17 which is sufficiently large to represent a spin glass or superparamagnetic state.[32] The broad nature of the $\chi'(T)$ and $\chi''(T)$ peaks suggests the presence of more than one transition. As hysteresis is usually observed below T_c, being that this is 2.3 K and that we are unable to obtain data below 2 K, hysteresis, which is expected at lower temperatures, was observed.[33]

Conclusion

An ETS of MnP based on a substituted TCNQ was prepared and structurally and magnetically characterized. The observed coordination motif of [DMTCNQ]$^{·-}$ is the first report of a *cis*-1,2-μ-bonding motif and produces a non-uniform zigzag 1-D chain.

Two types of non-uniform chains have been reported, Type-I and Type-II (Table 3), for [MnP][TCNE]. In Type-I each acceptor is located on a centre of symmetry and has a different orientation for the nearest neighbour acceptors in a chain.[8,34] For Type-II each acceptor does not lie on a centre of symmetry and although all acceptors are crystallographically identical, the bonding of the acceptor to each Mn is different.[28] The 1-D [Mn^{III}TMesP][DMTCNQ] chain is non-uniform and is classified as Type-II, unlike most [MnP][TCNE] complexes. Non-magnetically ordered complexes, *e.g.*, β-[MnPc][TCNE],[2,34] have large Δ values (Δ/Å = [bond a]−[bond b]). On the other hand, the value for a magnet having a strong intrachain exchange interaction, β-[MnTF$_4$OMePP][TCNE],[28] is quite

Table 2 XPS core IPs (eV) for [Mn^{III}TMesP][DMTCNQ]·2p-C$_6$H$_4$Me$_2$ and related compounds[a]

Compound	Cl$_{2p}$	C$_{1s}$	N$_{1s}$	Mn$_{2p\,3/2}$	Mn$_{2p\,1/2}$	Reference
[MnTMesp][DMTCNQ]		284.8	399.0	642.8	654.6	This work
[Mn^{II}TPP][C$_5$H$_5$N]		284.9	398.4	641.1	653.1	29
[Mn^{III}TPP]Cl	197.6	284.9	398.9	642.2	653.8	29
[Mn^{III}TPP][TCNE][C$_6$H$_5$Me]$_2$		284.9	399.1	642.6	654.2	29

[a]The spectrometer was calibrated so that the Au 4f$_{7/2}$ peak of the clean sputtered metals appeared at 84.0 eV. IPs are reproducible to a precision of ⩽±0.10 eV.

Table 3 Summary of structural features and magnetic properties of [MnP][acceptor] having non-uniform chain structures, Type-I and Type-II

bond b   bond a   bond b

Mn--N≡C—◯—C≡N--Mn--N≡C—◯—C≡N--Mn--N≡C—◯—C≡N--Mn

acceptor-I   MnP   acceptor-II   MnP   acceptor-I

Non-uniform Chain: Type-I

bond b bond a bond a   bond b bond b   bond a

Mn--N≡C—◯—C≡N--Mn--N≡C—◯—C≡N--Mn--N≡C—◯—C≡N--Mn

acceptor   MnP-I   acceptor   MnP-II   acceptor

Non-uniform Chain: Type-II

Compound	Type	Bond a/Å	Bond b/Å	Δ^a/Å	θ/K	T_c/K	Reference
[MnOEP][TCNE]^b	I	2.52	2.36	0.16	5	^{c}	8
β-[MnPc][TCNE]^b	I	2.42	2.34	0.08	12	^{c}	34
β-[MnTF$_4$OMePP][TCNE]^b	II	2.28	2.29	0.01	93	10.3	28
[MnTMesP][DMTCNQ]	II	2.35	2.32	0.03	23	2.3	This work

$^a\Delta$/Å = [bond a] − [bond b]. ^{b}See reference 2. ^{c}Paramagnetic behaviour, not magnetically ordered.

small, 0.01 Å. The value of [Mn^{III}TMesP][DMTCNQ] is intermediate and likewise has a moderate effective θ value, θ'. We conclude that a small difference between a and b bonds (Δ) gives a strong exchange interaction. Large Δ values result in very weak intrachain coupling evidenced by a small θ' value and low ordering temperatures.

Experimental

[Mn^{III}TMesP][DMTCNQ]·2-p-C$_6$H$_4$Me$_2$ was synthesized in a glove box with less than 1 ppm oxygen. A filtered hot solution of Mn^{II}TMesP·C$_5$H$_5$N^{13} (50.0 mg, 60 mmol) dissolved in 20 mL of boiling p-xylene was added to DMTCNQ (14.0 mg, 60 mmol: Tokyo Chemical Industry Co., Ltd.) dissolved in 20 mL of hot p-xylene. After standing overnight, the black-green crystals formed were harvested by vacuum filtration and dried under vacuum for 3 h (yield: 30.0 mg, 38%). Even after vacuum drying, elemental and thermogravimetric analysis indicated that the complex incorporates two p-xylene molecules. This value was used for diamagnetic correction. Calc. for C$_{86}$H$_{80}$MnN$_8$ (C$_{70}$H$_{60}$MnN$_8$·2C$_8$H$_{10}$): C, 80.66; H, 6.30; N, 8.75%. Found: C, 80.38, H, 6.11; N, 8.99%.

Crystal structure determination

Data were collected on a Rigaku AFC5R four circle diffractometer system with graphite monochromated Mo-Kα radiation (50 kV X 200 mA) equipped with a Rigaku low temperature device. The crystal was mounted on a top of glass fiber and placed quickly in the stream of cooled nitrogen, 208.0(3) K. The temperature was calibrated with an Anritsu HFT-50 thermometer. The measurement and structure analysis were performed by a package program available from Rigaku. Selected crystallographic information is given in Table 4. The crystal structure was solved by the direct method using SAPI91.^{35} Non-hydrogen atoms were refined anisotropically. CCDC reference number 1145/204. See http://www.rsc.org/suppdata/jm/a9/a907241a/ for crystallographic files in .cif format.

Table 4 Summary of the crystallographic data for [MnT^{III}MesPP]-[DMTCNQ]·2p-C$_6$H$_4$Me$_2$

Chemical formula	C$_{86}$H$_{80}$MnN$_8$
M_r	1280.57
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	15.460(5)
b/Å	16.781(7)
c/Å	15.429(6)
α/°	115.28(3)
β/°	90.88(3)
γ/°	90.88(3)
V/Å^3	3618(2)
Z	2
λ/Å	0.71069
ρ_{calcd}/g cm^{-3}	1.175
μ_{calcd}/cm^{-1}	2.33
R	0.076
R_w	0.093
Reflections measured/observed	12737/4618

Physical methods

The magnetic susceptibility was determined as previously reported.^{11} The diamagnetic correction for the disolvate (as determined by TGA) was calculated using Pascal's constants to be -832×10^{-6} emu mol^{-1}. The thermal properties were studied on a TA Instruments Model 2050 thermogravimetric analyzer (TGA, 38 to 1000 °C) placed in a Vacuum Atmospheres DriLab under argon. Samples were placed in an aluminum pan and heated to 450 °C at 15 °C min^{-1} under a continuous flow of nitrogen (10 mL min^{-1}). The infrared spectra were recorded on a Perkin-Elmer System-2000 FTIR spectrometer in the range of 650 to 4000 cm^{-1} on NaCl discs as a mineral oil mull. The XPS was performed on a KRATOS XSAM-800 equipped with a Mg anode X-ray gun ($h\nu = 1253.6$ eV). The spectrometer was calibrated so that the Au 4f$_{7/2}$ peak of the clean sputtered metals appeared at 84.0 eV. The detailed conditions of the XPS measurements were reported elsewhere.^{36}

Acknowledgements

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Paper a907241a