

Magnetic Behaviour of Octaethylporphyrinat manganese(III) Tetracyanoethenide, [MnOEP][TCNE], and Hexacyanobutadienide, [MnOEP][C₄(CN)₆]: The Importance of a Uniform Chain for Stabilizing Strong Effective Ferromagnetic Coupling

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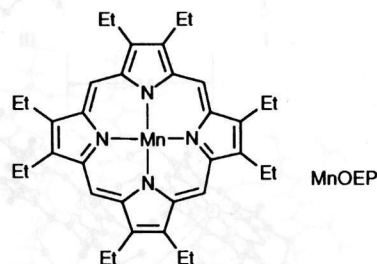
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[MnOEP][A] {A=[TCNE]^{•-} and [C₄(CN)₆]^{•-}} have been isolated as extended 1D coordination polymers with *trans*-μ₂-[A] bridging ligands with strong {A=[C₄(CN)₆]^{•-}} and weak {A=[TCNE]^{•-}} ferromagnetic coupling as evidenced from the fit of the magnetic susceptibility to the Curie-Weiss law ($\theta = 5.1$ and 67.1 K, respectively); the strong behaviour arises from the presence of uniform chains which are not present for the [TCNE]^{•-} salt.

The deliberate design and synthesis of molecule-based electron-transfer salts exhibiting cooperative magnetic^{1,2} as well as electrical behaviour⁴ is a growing area of contemporary interdisciplinary research. Recently, a new linear-chain structure type exemplified by the metallomacrocylic [MnTPP]^{•+}[TCNE]^{•-} (TPP=*meso*-tetraphenylporphyrinato) was reported to exhibit bulk magnetic properties.⁴ [MnTPP]^{•+}[TCNE]^{•-} is a covalently bonded, extended uniform 1D complex that was characterized to be a ferrimagnet with a T_c of 18 K; its magnetic susceptibility, χ , can be fitted to the Curie-Weiss expression, $\chi \propto (T - \theta)^{-1}$ between 115 and 250 K ($\theta = 61$ K).⁴ With the objectives of determining the structure-function relationship for this new class of materials and characterizing new molecule-based magnets with enhanced T_c s and θ s, we are exploring this class of compounds. Herein, we report the results of our studies of the reaction of TCNE and hexacyanobutadiene, C₄(CN)₆, with octaethylporphyrinat manganese(II), MnOEP.



MnOEP

The reaction of Mn^{II}OEPpy[†] with TCNE in toluene/MeCN led to the formation of [MnOEP]^{•+}[TCNE]^{•-}‡ and its

[†] Mn^{II}OEPpy was prepared by the reduction of [Mn^{III}OEP]Cl (Aldrich) with NaBH₄ with pyridine (py) in methanol by analogy to a literature method⁵ for [MnTPP]Cl (Method II). Mn^{II}OEP was prepared *via* the thermolysis of Mn^{II}OEPpy at 220 °C under high vacuum (*ca.* 5 × 10⁻⁵ Torr). Calc. for C₄₀H₄₄MnN₄ (Found) C=73.58 (72.86), H=7.54 (7.27) and N=9.54 (9.32)%. In contrast to Mn^{II}Pc (Pc=phthalocyanine) which is a canted ferromagnet with a critical temperature of 8.3 K (and $\theta = 23$ K), Mn^{II}OEP exhibits antiferromagnetic coupling with $\theta = -5.2$ K.⁶

‡ A solution of MnOEPpy (120 mg; 0.18 mmol) in toluene and a solution of TCNE (23 mg; 0.18 mmol) in MeCN were allowed to react at room temperature in an inert atmosphere glove box. Upon standing black crystals formed and were collected by vacuum filtration (110 mg; 85%). Infrared (Nujol) $\nu_{C\equiv N}$: 2126s, 2140m, and 2189m cm⁻¹. Calc. for C₄₂H₄₄MnN₈ (Found) C=70.49 (70.70), H=6.20 (6.28), N=15.66 (15.00) and Mn=7.68 (7.57)%.

reaction with C₄(CN)₆ in toluene led to the formation of [MnOEP]^{•+}[C₄(CN)₆]^{•-}§. Crystals of [MnOEP][TCNE]¶ and [MnOEP][C₄(CN)₆]* suitable for single-crystal X-ray diffraction were obtained from refrigerated toluene solutions.

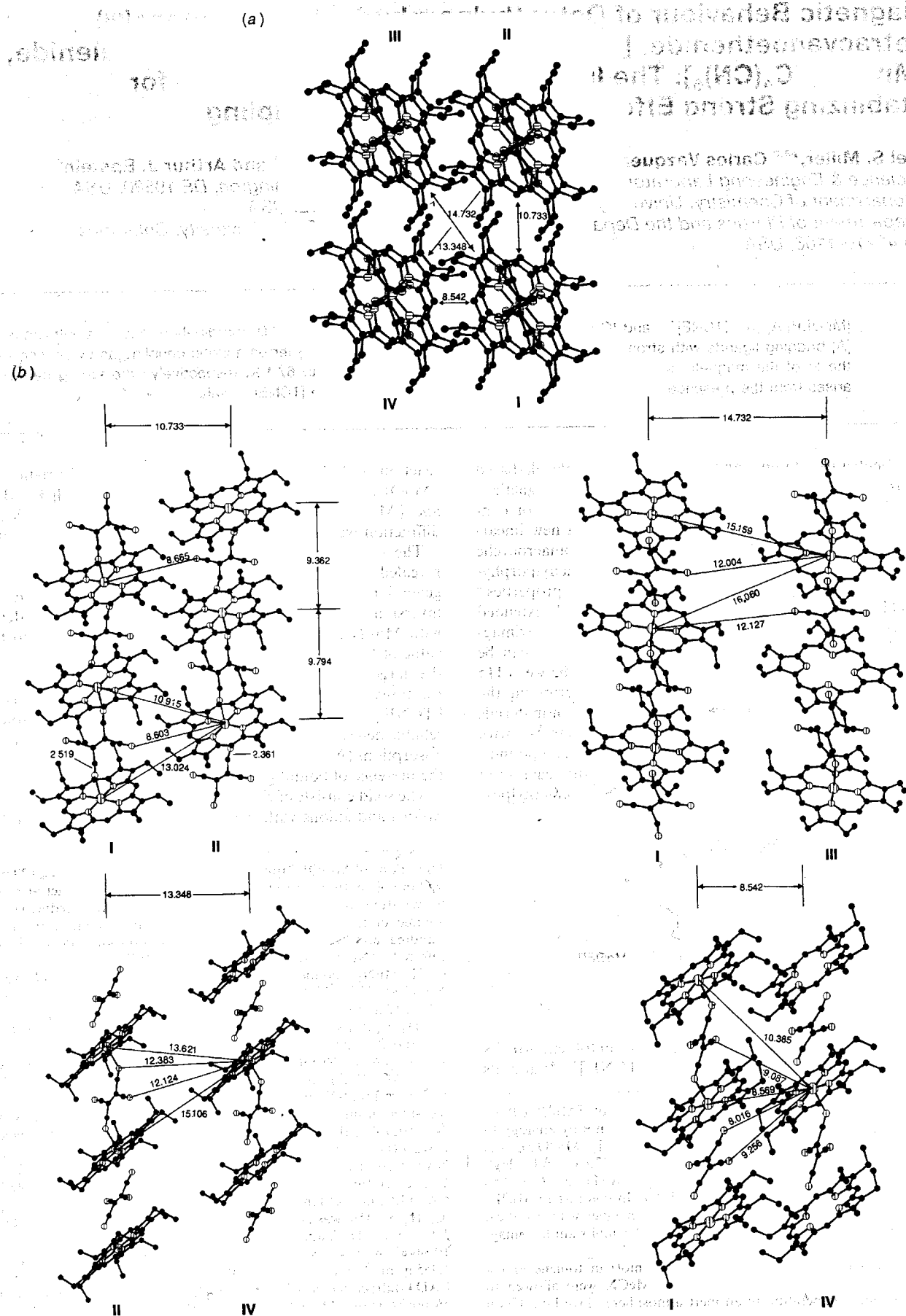
The -70 °C structure determination of [MnOEP][TCNE] revealed an asymmetric unit consisting of one cation in a general position and two half-anions each on independent inversion centres. The planar [Mn^{III}OEP]^{•+} cation is ordered with Mn-N distances of 1.997 Å. This is comparable to the value of 1.993 Å reported for [Mn^{III}TPP]^{•+}.⁴ The positions of the largest peaks in the final difference map suggests a rotational disorder about the inversion centres of both [TCNE]^{•-}s. This and the paucity of data do not enable a reliable determination of the central C-C distance. The $\nu_{C\equiv N}$ absorptions (Nujol) at 2126s, 2140m and 2189m cm⁻¹ confirm the presence of bound [TCNE]^{•-}, but not free [TCNE]^{•-}.⁷

The solid consists of chains of alternating covalently bonded cations and anions with the MnN₄ planes essentially parallel

§ Solutions of Mn(OEP)py (94 mg; 0.14 mmol) and C₄(CN)₆ (29 mg; 0.14 mmol) both dissolved in toluene were allowed to react at room temperature in an inert atmosphere glove box. After reducing the volume of the resultant solution to *ca.* 10 ml crystals formed on standing and were collected by vacuum filtration (85 mg; 77%). Infrared (Nujol) $\nu_{C\equiv N}$: 2139s and 2150s cm⁻¹. Calc. for C₄₆H₄₄MnN₁₀ (Found) C=69.78 (70.48, 68.86), H=5.40 (5.60, 5.51), N=17.81 (17.70, 17.22) and Mn=7.71 (6.94)%.

¶ A 0.17 mm × 0.10 mm × 0.56 mm crystal of [MnOEP][TCNE] (C₄₂H₄₄N₈Mn) was grown from toluene and belongs to the triclinic P1 (no. 2) space group; $a = 12.496(4)$ Å, $b = 13.024(5)$ Å, $c = 13.544(3)$ Å, $\alpha = 69.55(3)^\circ$, $\beta = 85.58(2)^\circ$, $\gamma = 64.48(3)^\circ$, $V = 1856.8$ Å³, $Z = 2$, $M = 715.81$, $\rho_{\text{calc}} = 1.280$ g cm⁻³; μ_{Mo} , 3.80 cm⁻¹ at -70 °C. Using an Enraf-Nonius CAD4 diffractometer, 6084 reflections were measured using graphite-monochromated Mo-K α radiation. With 445 variables, the structure was refined using 1935 data for which $I > 2.5\sigma(I)$ to convergence of $R = 0.074$ and $R_w = 0.052$. Crystal data have been deposited with the Cambridge Crystallographic Data Centre; see Information for Authors, *J. Mater. Chem.*, 1995, Table 1.

* A 0.10 mm × 0.18 mm × 0.43 mm crystal of [MnOEP][C₄(CN)₆] (C₄₆H₄₄N₁₀Mn) was grown from PhMe and belongs to the monoclinic P2₁/c (no. 14) space group; $a = 8.023(1)$ Å, $b = 22.636(4)$ Å, $c = 10.844(2)$ Å, $\beta = 99.89(1)^\circ$, $V = 1940.1$ Å³, $M = 791.87$, $Z = 2$; $\rho_{\text{calc}} = 1.355$ g cm⁻³; μ_{Mo} , 3.72 cm⁻¹ at -68 °C. Using an Enraf-Nonius CAD4 diffractometer, 4799 reflections were measured using graphite-monochromated Mo-K α radiation. With 259 variables, the structure was refined using 1423 data for which $I > 3\sigma(I)$ to convergence of $R = 0.056$ and $R_w = 0.049$. Crystal data have been deposited with the Cambridge Crystallographic Data Centre; see Information for Authors, *J. Mater. Chem.*, 1995, issue 1.



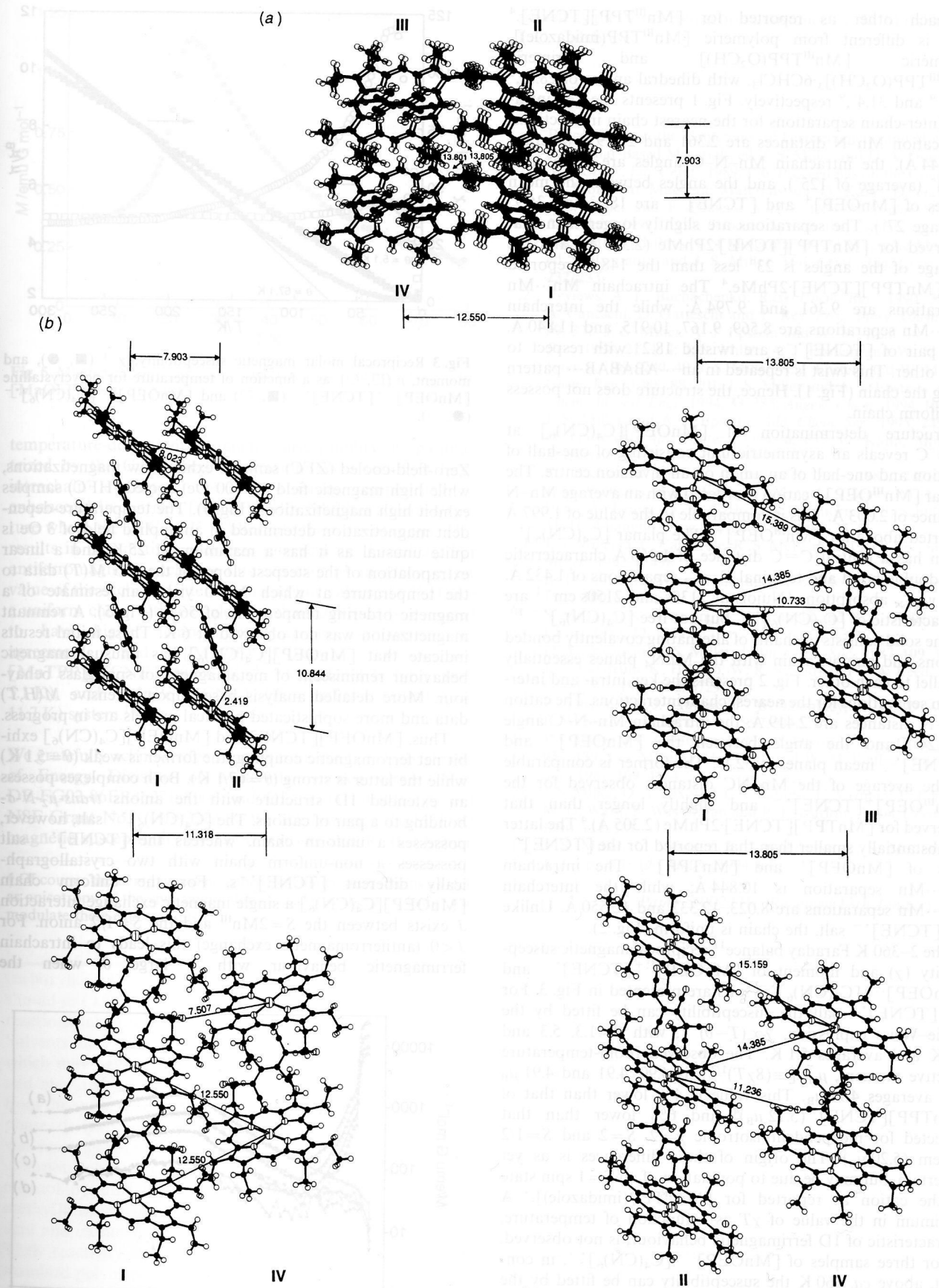


Fig. 2 View of unique chains: I, II, III and IV for $[\text{MnOEP}]^{3+}[\text{C}_4(\text{CN})_6]^{-}$. Note the $[\text{TCNE}]^{-}$ *trans*- μ_2 -*N*- σ -bonding to $[\text{MnOEP}]^{3+}$ and the uniform chains.

to each other as reported for $[\text{Mn}^{\text{III}}\text{TPP}][\text{TCNE}]$.⁴ This is different from polymeric $[\text{Mn}^{\text{III}}\text{TPP}(\text{imidazole})]$, polymeric $[\text{Mn}^{\text{III}}\text{TPP}(\text{O}_2\text{CH})]$ and trimeric $[\text{Mn}^{\text{III}}\text{TPP}(\text{O}_2\text{CH})_3 \cdot 6\text{CHCl}_3]$, with dihedral angles of 28.5°, 34.9° and 31.4°, respectively. Fig. 1 presents the key intra- and inter-chain separations for the nearest chain interactions. The cation Mn–N distances are 2.361 and 2.519 Å (average of 2.44 Å), the intrachain Mn–N–C angles are 117.6° and 132.4° (average of 125°), and the angles between the mean planes of $[\text{MnOEP}]^+$ and $[\text{TCNE}]^{2-}$ are 18.2° and 35.9° (average 27°). The separations are slightly longer than that observed for $[\text{MnTPP}][\text{TCNE}] \cdot 2\text{PhMe}$ (2.305 Å), and the average of the angles is 23° less than the 148.1° reported for $[\text{MnTPP}][\text{TCNE}] \cdot 2\text{PhMe}$.⁴ The intrachain Mn...Mn separations are 9.361 and 9.794 Å; while the interchain Mn...Mn separations are 8.569, 9.167, 10.915, and 11.840 Å. The pair of $[\text{TCNE}]^{2-}$ s are twisted 18.2° with respect to each other. This twist is repeated in an ...ABABAB... pattern along the chain (Fig. 1). Hence, the structure does not possess a uniform chain.

Structure determination of $[\text{MnOEP}][\text{C}_4(\text{CN})_6]$ at -68°C reveals an asymmetric unit consisting of one-half of a cation and one-half of an anion on an inversion centre. The planar $[\text{Mn}^{\text{III}}\text{OEP}]^+$ cation is ordered with an average Mn–N distance of 2.003 Å. This is comparable to the value of 1.997 Å reported above for $[\text{Mn}^{\text{III}}\text{OEP}]^+$. The planar $[\text{C}_4(\text{CN})_6]^{2-}$ anion has a central C=C distance of 1.366 Å characteristic of a double bond and terminal C–C₃ separations of 1.432 Å. The $\nu_{\text{C}\equiv\text{N}}$ absorptions (Nujol) at 2139s and 2150s cm^{-1} are characteristic of $[\text{C}_4(\text{CN})_6]^{2-}$, but not free $[\text{C}_4(\text{CN})_6]^{2-}$.¹⁰

The solid consists of chains of alternating covalently bonded cations and anions, again with the MnN_4 planes essentially parallel to each other. Fig. 2 presents the key intra- and inter-chain separations for the nearest chain interactions. The cation Mn–N distances are 2.419 Å, the intrachain Mn–N–C angle is 124°, and the angle between the $[\text{MnOEP}]^+$ and $[\text{TCNE}]^{2-}$ mean planes is 32.1°. The former is comparable to the average of the Mn–NC distances observed for the $[\text{Mn}^{\text{III}}\text{OEP}]^+[\text{TCNE}]^{2-}$ and slightly longer than that observed for $[\text{MnTPP}][\text{TCNE}] \cdot 2\text{PhMe}$ (2.305 Å).⁴ The latter is substantially smaller than that reported for the $[\text{TCNE}]^{2-}$ salts of $[\text{MnOEP}]^+$ and $[\text{MnTPP}]^+$. The intrachain Mn...Mn separation is 10.844 Å; while the interchain Mn...Mn separations are 8.023, 12.332 and 12.550 Å. Unlike the $[\text{TCNE}]^{2-}$ salt, the chain is uniform (Fig. 2).

The 2–360 K Faraday balance¹¹ reciprocal magnetic susceptibility (χ) and moment of $[\text{MnOEP}]^{2+}[\text{TCNE}]^{2-}$ and $[\text{MnOEP}]^{2+}[\text{C}_4(\text{CN})_6]^{2-}$ salts are presented in Fig. 3. For the $[\text{TCNE}]^{2-}$ salt the susceptibility can be fitted by the Curie–Weiss expression, $\chi \propto (T-\theta)^{-1}$, with $\theta = 1.3$, 5.3 and 8.8 K and averages 5.1 K. The observed room-temperature effective moment, $\mu_{\text{eff}} [\equiv (8\chi T)^{1/2}]$, is 4.90, 4.91 and 4.91 μ_{B} and averages 4.91 μ_{B} . This value is 4% lower than that of $[\text{MnTPP}][\text{TCNE}]$ (5.12 μ_{B})⁴ and 6% lower than that expected for independent isotropic $g=2$, $S=2$ and $S=1/2$ system (5.20 μ_{B}). The origin of these differences is as yet uncertain, but may be due to population of an $S=1$ spin state of the cation as reported for $[\text{Mn}^{\text{III}}\text{TPP}(\text{imidazole})]$.⁹ A minimum in the value of χT as a function of temperature, characteristic of 1D ferrimagnetic behaviour, is not observed.

For three samples of $[\text{MnOEP}]^{2+}[\text{C}_4(\text{CN})_6]^{2-}$, in contrast, above ca. 160 K the susceptibility can be fitted by the Curie–Weiss expression with $\theta = 65.4$, 66.4 and 69.9 K [averaging 67.1(2.4) K] (Fig. 3). The observed room-temperature effective moments are 4.73, 4.25 and 4.60 μ_{B} and average 4.53 μ_{B} . Field-dependent behaviour is observed below ca. 50 K independent of the history of the sample. Below 8 K the magnetization is dependent on magnetic and thermal history.

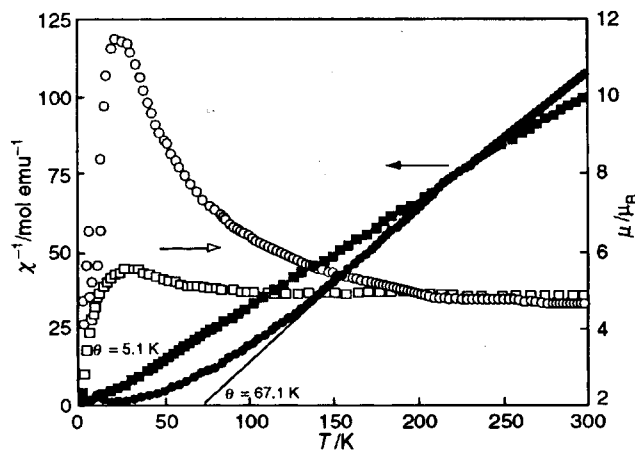


Fig. 3 Reciprocal molar magnetic susceptibility, χ^{-1} (■, ●), and moment, μ (□, ○), as a function of temperature for polycrystalline $[\text{MnOEP}]^{2+}[\text{TCNE}]^{2-}$ (■, □) and $[\text{MnOEP}]^{2+}[\text{C}_4(\text{CN})_6]^{2-}$ (●, ○).

Zero-field-cooled (ZFC) samples exhibit low magnetizations, while high magnetic field (19 500 Oe) cooled (HFC) samples exhibit high magnetizations (Fig. 4). The temperature-dependent magnetization determined in an applied field of 3 Oe is quite unusual as it has a maximum at 25 K and a linear extrapolation of the steepest slopes of the 3 G $M(T)$ data to the temperature at which $M=0$ yields an estimate of a magnetic ordering temperature of 56 K (Fig. 5). A remnant magnetization was not observed at 6 K. These initial results indicate that $[\text{MnOEP}][\text{C}_4(\text{CN})_6]$ has unusual magnetic behaviour reminiscent of metamagnetic or spin-glass behaviour. More detailed analysis based upon extensive $M(H, T)$ data and more sophisticated physical models are in progress.

Thus, $[\text{MnOEP}][\text{TCNE}]$ and $[\text{MnOEP}][\text{C}_4(\text{CN})_6]$ exhibit net ferromagnetic coupling; the former is weak ($\theta = 5.1$ K) while the latter is strong ($\theta = 67.1$ K). Both complexes possess an extended 1D structure with the anions *trans*- μ_2 -N- σ -bonding to a pair of cations. The $[\text{C}_4(\text{CN})_6]^{2-}$ salt, however, possesses a uniform chain, whereas the $[\text{TCNE}]^{2-}$ salt possesses a non-uniform chain with two crystallographically different $[\text{TCNE}]^{2-}$ s. For the uniform chain $[\text{MnOEP}][\text{C}_4(\text{CN})_6]$ a single magnetic exchange interaction J exists between the $S=2\text{Mn}^{\text{III}}$ and the $S=1/2$ anion. For $J < 0$ (antiferromagnetic exchange) this leads to intrachain ferrimagnetic behaviour with a large θ when the

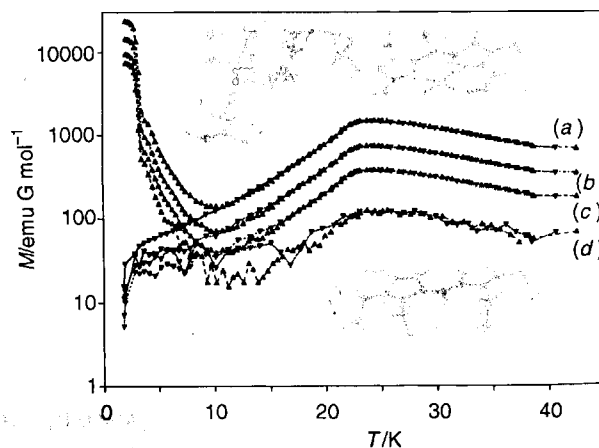


Fig. 4 Zero-field (▼) and high-field-cooled (Δ) magnetization for $[\text{MnOEP}]^{2+}[\text{C}_4(\text{CN})_6]^{2-}$ as a function of temperature. (a) 150, (b) 500, (c) 1000, (d) 2000 G.

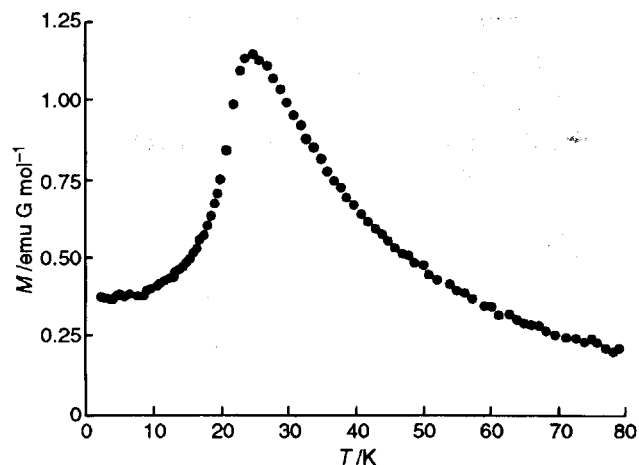


Fig. 5 Magnetization as a function of temperature for $[\text{MnOEP}]^{3+}[\text{C}_4(\text{CN})_6]^{3-}$

temperature-dependent magnetic susceptibility is parametrized by the Curie-Weiss expression. As a result of large intrachain exchange, the 3D ordering temperature is enhanced.† In contrast, $[\text{MnOEP}][\text{TCNE}]$ has a chain structure where the $[\text{TCNE}]^-$ s alternate their orientations. This results in two distinct exchange interactions, J_1 and J_2 . For antiferromagnetic exchange this can lead to an effective low value of the exchange interaction and low values of θ .¹¹ Hence a uniform chain with a single intrachain J would be expected to have higher temperature magnetic phenomena, in agreement and $[\text{MnOEP}][\text{C}_4(\text{CN})_6]$ ($\theta = 67.1$ K), $[\text{MnTPP}][\text{TCNE}]$ ($\theta = 61$ K),⁴ $[\text{MnOEP}][\text{TCNE}]$ ($\theta = 5.1$ K), and $[\text{MnPc}][\text{TCNE}]$ (Pc = phthalocyanine) ($\theta = 11.7$ K) system.¹²

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† Of course, the next-nearest neighbour exchange interactions as well as anisotropy of the spin interactions (e.g., Heisenberg vs. Ising) will modulate these expectations.

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