Magnetic Ordering of 5,10,15,20-Tetrakis[4'-(trifluoromethyl)phenyl]-porphyrinatomanganese(III) Tetracyanoethenide with a 6.0 K T_c

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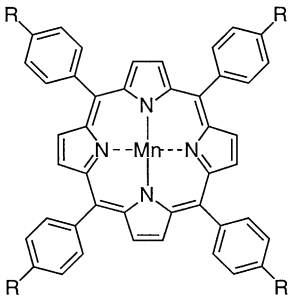
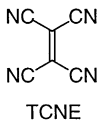
An electron-transfer complex of a substituted manganese porphyrin with tetracyanoethylene was prepared. Crystal structure analysis revealed that there exists quasi-two dimensional interaction in the complex, which was shown to be a magnet with T_c of 6.0 K.

Electron-transfer complexes constructed from manganese(II) porphyrins and acceptors with cyano groups such as tetracyanoethylene (TCNE) produce coordination complexes with extended linear-chain one dimensional (1-D) structure which display strong antiferromagnetic coupling and ferrimagnetic behavior below an ordering temperature.[1-5] Although some derivatives of porphyrins have been studied,[6,7] the relationships between the structure and the magnetism are still unclear.[5] In order to determine the structure-function relationship for this new class of materials, we introduced trifluoromethyl (CF_3) groups onto the phenyl groups of TPP with a hope that the substituents may alter the molecular alignment in the crystal.[8,9] In this communication, we wish to report the synthesis, crystal structure, and magnetic properties of [Mn(III)TCF_3PP][TCNE], in which the interaction between the 1-D chains is controlled by the van der Waals contacts of fluorine atoms.





The manganese complex of TCF_3PP was prepared from the corresponding free base according to the method previously reported.[2,8,10,11] The direct redox reaction between [Mn(II)TCF_3PP] and TCNE in chlorobenzene (PhCl) was performed in an inert atmosphere in a glove box. Stoichiometry of the complex was determined to be [Mn(III)TCF_3PP][TCNE][PhCl]$_2$ on the basis of elemental analysis and crystal structure analysis.[12,13] The following evidences support the electronic structure of this complex as an ionic ground state salt, *i.e.*, exactly one electron transferred from manganese(II) metal to TCNE molecule to yield $S = 2$ for [Mn(III)TCF_3PP]$^+$ and $S = 1/2$ for [TCNE]$^{-\bullet}$. First, the central C=C bond distance of TCNE is 1.43(1) Å and is comparable to that of reported TCNE anion radicals.[14] Second, metal centered oxidation potential of [Mn(II)TCF_3PP], -0.08 V, is lower than the first reduction potential of TCNE, +0.28 V.[11] This energy gap is expected to produce an ionic ground state complex.[15] Third, the vibration spectrum is the superimposed of TCNE anion radical and [Mn(III)TCF_3PP]Cl. The bands of ν_{CN} at 2205 and 2163 cm^{-1} are shifted to higher frequency compared to those of non-coordinated TCNE anion radical at 2183 and 2144 cm^{-1}.[14] These shifts indicate the presence of Mn-N coordination bond[2,5] and are consistent with the crystallographic study (*vide infra*).

The crystal structure of the complex is shown in Figures 1 and 2. Two nitrogen atoms of the [TCNE]$^{-\bullet}$ coordinate to manganese with the bond distance of 2.300(6) Å. The manganese site and TCNE molecules are located on the inversion centers of $P\bar{1}$ space group. Like [Mn(III)TPP][TCNE], a uniform 1-D chain is observed.[2] The largest difference between the two complexes is the dihedral angle between the porphyrin and TCNE planes: 75.4° for [Mn(III)TCF_3PP][TCNE] and 55.3° for [Mn(III)TPP][TCNE]. The 1-D chain of the present complex is closely packed in that the *out-of-registry* manner and produces a quasi two-dimensional (2-D) sheet structure (Figure 1). The

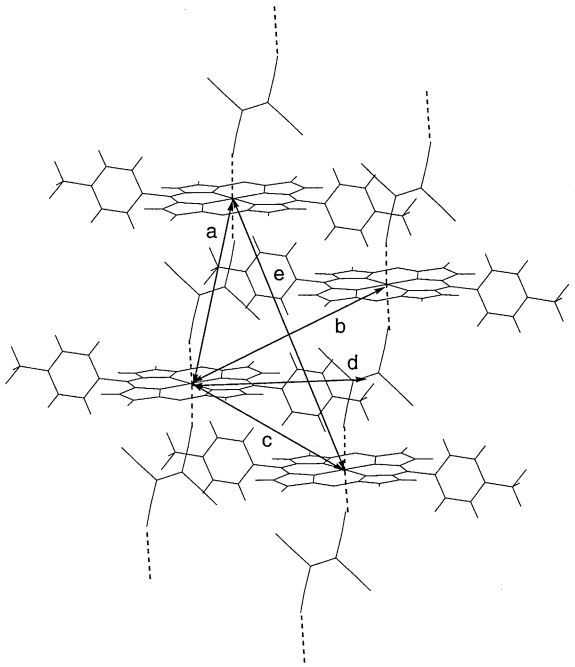


Figure 1. *Out-of-registry* packing structure of the complex. For clarity, solvent molecules, front and behind phenyl groups of $MnTCF_3PP$ were omitted. Mn-N coordination bonds, 2.300(6) Å, are indicated by dotted lines. Mn-Mn and Mn-TCNE interactions are indicated by arrows: 10.22 (a), 11.93 (b), 9.78 (c), 9.64 (d), and 16.06 Å (e).

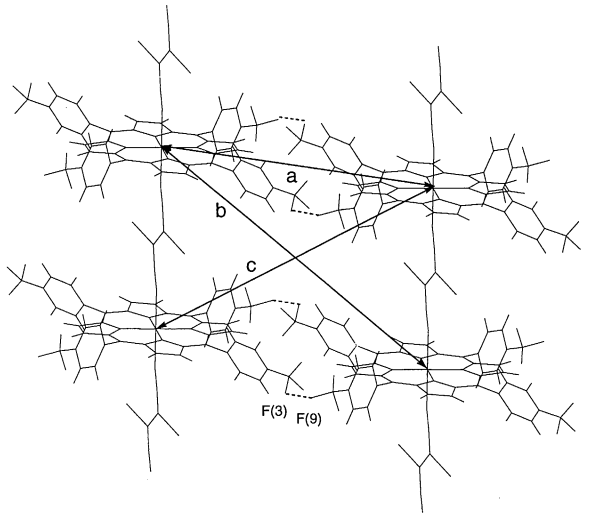


Figure 2. *In-registry* packing structure of the complex. For clarity, solvent molecules were omitted. Interchain fluorine-fluorine close contacts, 2.924(9) Å, are indicated by dotted lines. Mn-Mn interactions are indicated by arrows: 15.46 (a), 19.48 (b), and 17.54 Å (c).

shortest distance between Mn metal and the centroid of $[TCNE]^{-\bullet}$ is 9.64 Å. This value is much shorter (0.60 Å) than the corresponding value for [Mn(III)TPP][TCNE], 10.24 Å.[2] The quasi 2-D sheets are separated by the CF_3 groups of TCF_3PP in the [010] directions (Figure 2). An intermolecular F(3)-F(6) separation was found to be 2.924(9) Å and is comparable to the sum of van der Waals radii for fluorine atoms (2.94 Å).[16] The larger interchain Mn-Mn distances (15.46, 17.54, and 19.48 Å for the present complex, 12.49, 17.14, and 14.93 Å for [Mn(III)TPP][TCNE]) is attributed to the substituent.[2]

The susceptibility (χ) of the complex obeys the Curie-Weiss equation, $\chi = 1 / (T-\theta)$, above 200 K where θ is -33 ± 1 K and between 70-130 K with an effective θ of $+33 \pm 2$ K. The observed effective moment is 4.92 μ_B at 300 K in good agreement with the value obtained for [Mn(III)TPP][TCNE] (5.12 μ_B).[2] The value is consistent with those expected for independent isotropic $g = 2$, $S = 2$, and $S = 1/2$ systems (5.20 μ_B) with strong antiferromagnetic coupling. A minimum in $\chi T(T)$ characteristic of 1-D antiferromagnetic coupling is observed at 160 K. The χ value has the maximum at 10 K. In order to observe long range magnetic ordering, AC susceptibility measurements (10, 100, and 1000 Hz) were performed. The in-phase component, χ', shows a sharp maximum at 6.0 K attributable to the ordering temperature of the material. Due to the decrease of *in-registry* interaction, the T_c of the complex is much lower than that previously reported for [Mn(III)TPP][TCNE] (18.0 K).[2]

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11 Selected data of $[Mn(II)TCF_3PP]$ pyridine complex are the followings: UV-vis. (pyridine, qualitative): 614, 574, and 443 nm; Redox potentials (PhCN, $TBAPF_6$, *vs.* Ag / AgCl): +1.54, -0.08 (Mn(III) / Mn(II)), -1.45, and -1.86 V.
12 Crystal data for $[Mn(III)TCF3PP][TCNE][PhCl]_2$: $C_{66}H_{34}Cl_2F_{12}N_8Mn$, FW = 1292.87, triclinic, $P\bar{1}$ (#2), 0.88 X 0.38 X 0.01 mm^3, -44.4±1.0 °C, Mo-K_α, a = 10.223(4), b = 15.462(6), c = 9.779(4) Å, α = 99.45(3), β = 106.79(3), γ = 83.47(3)°, V = 1456(1) $Å^3$, Z = 1, R = 0.095, Rw = 0.094 for 2746 independent reflections ($I>3.00\sigma(I)$).
13 Some incorporated solvent molecules of the complex were lost by vacuum drying. The samples for magnetic measurement were dried under vacuum for overnight. Thermogravimetry analysis indicates that the sample contains 1.8 PhCl molecules. This value was used for diamagnetic correction.
14 The corresponding values of [Mn(III)TPP][TCNE] and $[Fe(C_5Me_5)_2][TCNE]$ are 1.369(10)[2] and 1.392(9) Å, respectively. J. S. Miller, J. C. Calabrese, H. Rommelmann, S. R. Chittipeddi, J. H. Zhang, W. M. Reiff, and A. J. Epstein, *J. Am. Chem. Soc.*, **109**, 769 (1987).
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