

# First Isolation and Characterization of an Electron Transfer Salt of a Tetracyanoquinodimethane with Porphyrinatomanganese(II) Having Novel *cis*- $\mu$ -Coordination Manner: A Molecule-based Magnet with a 2.3 K $T_c$

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An electron transfer salt comprised of 2,5-dimethyl-7,7,8,8-tetracyano-*p*-quinodimethane (DMTCNQ) with porphyrinatomanganese(II) was structurally and magnetically characterized. The  $[\text{DMTCNQ}]^{\bullet}$  exhibits a novel *cis*- $\mu$ -coordination motif.

Polymeric electron-transfer (ET) salts constructed from porphyrinatomanganese(II) ( $[\text{MnP}]$ ) and a strong electron acceptor such as tetracyanoethylene (TCNE)<sup>1,2</sup> have attracted much attention due to the observation of bulk ferrimagnetic ordering.<sup>3</sup> To gain a deeper understanding of these magnets, new acceptors that can stabilize ferrimagnetic ordering are sought. Several groups have replaced TCNE with  $\pi$ -expanded 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) **1a**, however, no information concerning the structure of these complexes is available and therefore, a detailed understanding on the magnetism is lacking.<sup>4</sup> Recently, we reported the unprecedented honeycomb supramolecular structure as a product of **1a** and *meso*-tetrakis(2,4,6-trimethylphenyl)porphyrinatomanganese(II), **2a**, however, the diamagnetic dimerized dianion of **1a** displayed no magnetic ordering.<sup>5</sup> Herein, we report the first isolation and characterization of an ET salt of a substituted TCNQ, 2,5-dimethyl-7,7,8,8-tetracyano-*p*-quinodimethane, **1b**, with **2a** having a novel *cis*- $\mu$ -coordination.

The reaction of **2a**<sup>5</sup> and **1b** in *p*-xylene led to the isolation of  $[\text{2a}][\text{1b}] \cdot 2p$ -xylene.<sup>6</sup> X-Ray photoelectron spectroscopy reveals Mn core ionization potentials of 642.8 eV for  $\text{Mn}2\text{p}_{3/2}$  and 654.6 eV for  $\text{Mn}2\text{p}_{1/2}$  characteristic of hexacoordinated Mn<sup>III</sup>.<sup>7,8</sup> The  $\nu_{\text{CN}}$  values of the  $[\text{2b}][\text{1b}]$  (2184 and 2160 cm<sup>-1</sup>)

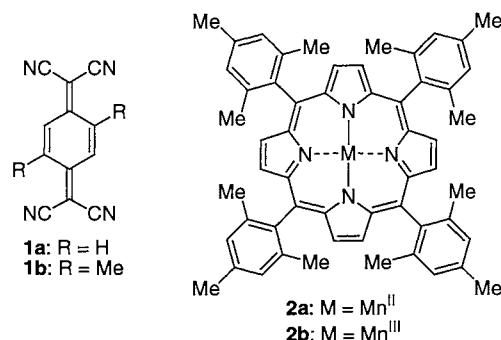


Figure 1.

are shifted to lower energy from the 2223 and 2212 cm<sup>-1</sup> observed for **1b** consistent with reduction of **1b** to  $[\text{1b}]^{\bullet}$ . The IR data and the observed bond lengths of **1b** (*vide infra*) support one electron transfer from Mn<sup>II</sup> to **1b** yielding  $S = 2$  for  $[\text{2b}]^+$  and  $S = 1/2$  for  $[\text{1b}]^{\bullet}$ .

X-Ray analysis<sup>9</sup> revealed that  $[\text{2b}][\text{1b}]$  forms one-dimensional (1-D) chains comprised of alternating  $[\text{2b}]^+$  and  $[\text{1b}]^{\bullet}$  with each Mn<sup>III</sup> being hexacoordinate *cis*- $\mu$ -N-bound to two  $[\text{1b}]^{\bullet}$ 's (Figure 2). This 1-D coordination polymeric motif has been observed for most magnetically ordered  $[\text{MnP}][\text{TCNE}]$  complexes.<sup>1,2</sup> Each  $[\text{1b}]^{\bullet}$  bonds to two Mn<sup>III</sup>'s in a *cis*-manner. This is the first report of this novel coordination geometry.<sup>1,3,4</sup> The  $[\text{1b}]^{\bullet}$  is nonplanar as the characteristic bond alternation usually seen for quinoids is lost consistent with its anionic nature. Furthermore, the increased single bond character of exo

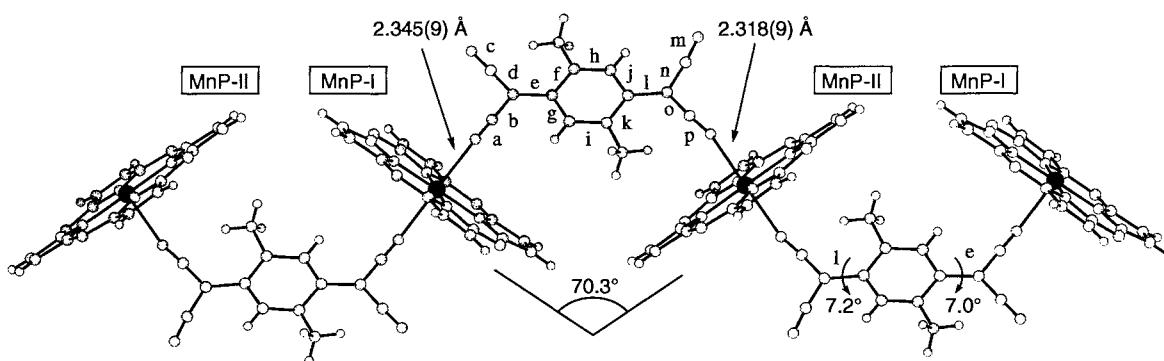
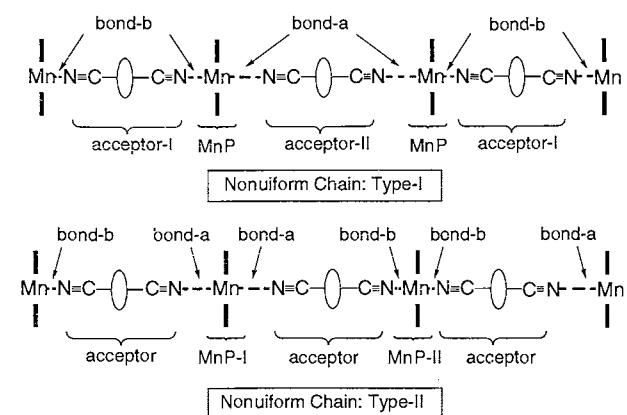


Figure 2. A segment of the 1-D chain structure. For clarity, solvent molecules and aryl groups of  $[\text{2b}]^+$  were omitted. Only Mn<sup>III</sup> is located on the inversion center of  $P\bar{1}$  space group. Intramolecular bond distances of  $[\text{1b}]^{\bullet}$  are the following: a: 1.14, b: 1.44, c: 1.14, d: 1.39, e: 1.43, f: 1.46, g: 1.39, h: 1.36, i: 1.39, j: 1.40, k: 1.43, l: 1.45, m: 1.14, n: 1.41, o: 1.41, and p: 1.17 Å. The mean Mn-N(**2b**) distances are 2.001 and 1.996 Å for MnP-I and MnP-II, respectively.

**Table 1.** Summary of structural features and magnetic properties of  $[\text{MnP}][\text{acceptor}]$  having nonuniform chain structures, Type-I and Type-II.



	Type	bond-a ( $\text{\AA}$ )	bond-b ( $\text{\AA}$ )	$\Delta^a$ ( $\text{\AA}$ )	$\theta$ (K)	$T_c$ (K)	Ref.
$[\text{MnOEP}][\text{TCNE}]^b$	I	2.52	2.36	0.16	5	c)	10
$\beta\text{-}[\text{MnPc}][\text{TCNE}]^b$	I	2.42	2.34	0.08	12	c)	11
$\beta\text{-}[\text{MnTF}_4\text{OMePP}][\text{TCNE}]^b$	II	2.28	2.29	0.01	93	10.3	12
<b>[2b][1b]</b>	II	2.35	2.32	0.03	23	2.3	d)

<sup>a</sup>  $\Delta$  ( $\text{\AA}$ ) = [bond-a] - [bond-b]. <sup>b</sup> OEP: octaethylporphyrinato, Pc: phthalocyanato, TF<sub>4</sub>OMePP: *m*eso-tetrakis(2,3,5,6-tetrafluoro-4-methoxyphenyl)porphyrinato. <sup>c</sup> Paramagnetic behaviour, not magnetically ordered. <sup>d</sup> This work, see Ref. 13.

methylene bonds enable about 7° rotations of dicyanomethylene units toward the central six-membered ring around bond-e and bond-l, Figure 2.

Two types of nonuniform chains have been reported, Type-I and Type-II (Table 1). Type-I has each acceptor on a center of symmetry and different orientations for nearest neighbor acceptors in a chain,<sup>10,11</sup> while each acceptor does not lie on a center of symmetry for Type-II and although all acceptors are the same, the bonding of an acceptor is different to each Mn it bonds.<sup>12</sup> The 1-D [2b][1b] chain is nonuniform and is classified into Type-II, as unlike most  $[\text{MnP}][\text{TCNE}]$  complexes.<sup>1,2</sup> The Mn-N<sub>1b</sub> distances are 2.345(9) and 2.318(9)  $\text{\AA}$ .<sup>13</sup> The dihedral angles between [1b]<sup>•</sup> and porphyrin planes are 56.8° and 49.0° for MnP-I<sup>•</sup>•[1b]<sup>•</sup> and MnP-II<sup>•</sup>•[1b]<sup>•</sup>, respectively. The dihedral angle between the two adjacent porphyrin rings in the chain is 70.3° which is the largest value comparing with those for reported 1-D  $[\text{MnP}]$  salts,<sup>14</sup> but different from the parallel alignment of  $[\text{MnP}][\text{TCNE}]$ .<sup>1,2</sup>

The susceptibility ( $\chi$ ) of the complex obeys the Curie-Weiss equation,  $\chi = 1 / (T - \theta)$ , where  $\theta$  is  $-10 \pm 1$  K ( $130 < T < 250$  K), and  $+23 \pm 1$  K ( $T > 250$  K). The observed effective moment is  $5.10 \mu_B$  at 300 K, which is in good agreement with the value ( $5.20 \mu_B$ ) expected for independent isotropic  $g = 2$ ,  $S = 2$  of Mn<sup>III</sup> and  $S = 1/2$  of [1b]<sup>•</sup> systems. A minimum in  $\chi T(T)$  characteristic of 1-D antiferromagnetic coupling is observed at 115 K. The  $\chi(T)$  value has the maximum at 10 K. The in-phase component,  $\chi'(T)$ , of an AC susceptibility measurements shows a sharp maximum at 2.3 K attributable to the ordering temperature ( $T_c$ ) of the material. The studies of TCNQ based  $[\text{MnP}]$  ET salts having uniform chain structures are now in

progress.

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- 6 Complex formation reactions were carried out in a glove box with less than 1 ppm oxygen. A filtered hot solution of **2a**<sup>5</sup> (50.0 mg, 60 mmol) dissolved in 20 mL of boiling *p*-xylene was added to **1b** (14.0 mg, 60 mmol; TCI Co., Ltd) dissolved in 20 mL of hot *p*-xylene. After standing for overnight, black-green crystals formed and were harvested by vacuum filtration and dried under vacuum for 3 h, 30.0 mg (38%). Even after a vacuum drying, elemental analysis and thermogravimetry analysis indicates that the sample incorporates two *p*-xylene molecules. This value was used for diamagnetic correction. Anal. Calcd for  $C_{102}H_{100}Mn_1N_8$ : C, 80.66; H, 6.30; N, 8.75%. Found: C, 80.38, H, 6.11; N, 8.99%.
- 7 The spectrometers were calibrated so that the Au4f<sub>7/2</sub> peak of the clean sputtered metals appeared at 84.0 eV. IPs are reproducible to a precision of  $\leq \pm 0.10$  eV. C1s = 284.8, N1s = 399.0 Mn2p<sub>3/2</sub> = 642.8 and Mn2p<sub>1/2</sub> = 654.6 eV.
- 8 K.-i. Sugiura, S. Mikami, K. Iwasaki, S. Hino, E. Asato, and Y. Sakata, *J. Org. Chem.*, **1999**, submitted; for hexacoordinated Mn<sup>III</sup> salt ( $[\text{Mn}^{\text{III}}\text{TPP}][\text{TCNE}]$ ): Mn2p<sub>3/2</sub> = 642.6 and Mn2p<sub>1/2</sub> = 654.2 eV, for pentacoordinated Mn<sup>III</sup> salt ( $[\text{Mn}^{\text{III}}\text{TPP}]\text{Cl}$ ): 642.2 and 653.8 eV, for pentacoordinated Mn<sup>II</sup> salt ( $[\text{Mn}^{\text{II}}\text{TPP}][\text{pyridine}]$ ): 641.1 and 653.1 eV.
- 9 Crystal data for  $C_{86}H_{80}MnN_8$  {[2b][1b]}<sup>2p-Xylene</sup>,  $Z = 2$ ,  $M = 1280.57$ , triclinic  $P\bar{1}$  (#2) space group:  $a = 15.460(5)$   $\text{\AA}$ ,  $b = 16.781(7)$   $\text{\AA}$ ,  $c = 15.429(6)$   $\text{\AA}$ ,  $\alpha = 115.28(3)$ °,  $\beta = 90.876(31)$ °,  $\gamma = 90.881(33)$ °,  $V = 3618(2)$   $\text{\AA}^3$ ,  $\rho_c = 1.175$  g  $\text{cm}^{-3}$ ,  $\lambda = 0.71070$   $\text{\AA}$ ,  $T = -65 \pm 1$  °C,  $2\theta_{\text{max}} = 50.0$ °,  $R(R_w) = 0.076$  (0.093), Goodness-of-Fit = 1.38, reflection-parameter ratio = 5.37 based on 4618 unique reflections with  $I > 3\sigma(I)$ . Data were collected on a Rigaku AFC5R four circled diffractometer system with a graphite monochromated Mo-K $\alpha$  radiation (50 KV X 200 mA) and the structure was solved by a teXsan crystallographic software package from Rigaku.
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