

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

Ken-ichi Sugiura, Shinji Mikami, Mitchell T. Johnson,[†] Joel S. Miller,[†]

Kentaro Iwasaki,^{††} Kazunori Umishita,^{††} Shojun Hino,^{††} and Yoshiteru Sakata*

The Institute of Scientific and Industrial Research (ISIR), Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047

[†]Department of Chemistry, University of Utah, Salt Lake City, UT 84112-0850, U.S.A.

^{††}Faculty of Engineering, Chiba University, Inage-ku, Chiba 263-8522

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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 [DMTCNQ]^{-•} exhibits a novel *cis*- μ -coordination motif.

Polymeric electron-transfer (ET) salts constructed from porphyrinatomanganese(II) ([MnP]) and a strong electron acceptor such as tetracyanoethylene (TCNE)^{1,2} have attracted much attention due to the observation of bulk ferrimagnetic ordering.³ To gain a deeper understanding of these magnets, new acceptors that can stabilize ferrimagnetic ordering are sought. Several groups have replaced TCNE with π -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.⁴ 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.⁵ 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*- μ -coordination.

The reaction of **2a** and **1b** in *p*-xylene led to the isolation of [2a][1b]·2*p*-xylene.⁶ X-Ray photoelectron spectroscopy reveals Mn core ionization potentials of 642.8 eV for Mn2p_{3/2} and 654.6 eV for Mn2p_{1/2} characteristic of hexacoordinated Mn^{III}.^{7,8} The ν_{CN} values of the [2b][1b] (2184 and 2160 cm⁻¹)

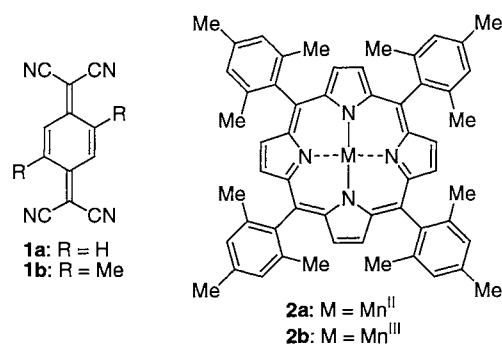


Figure 1.

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

X-Ray analysis⁹ revealed that [2b][1b] forms one-dimensional (1-D) chains comprised of alternating [2b]⁺ and [1b]^{-•} with each Mn^{III} being hexacoordinate *cis*- μ -N-bound to two [1b]^{-•}s (Figure 2). This 1-D coordination polymeric motif has been observed for most magnetically ordered [MnP][TCNE] complexes.^{1,2} Each [1b]^{-•} bonds to two Mn^{III}s in a *cis*-manner. This is the first report of this novel coordination geometry.^{1,3,4} The [1b]^{-•} 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

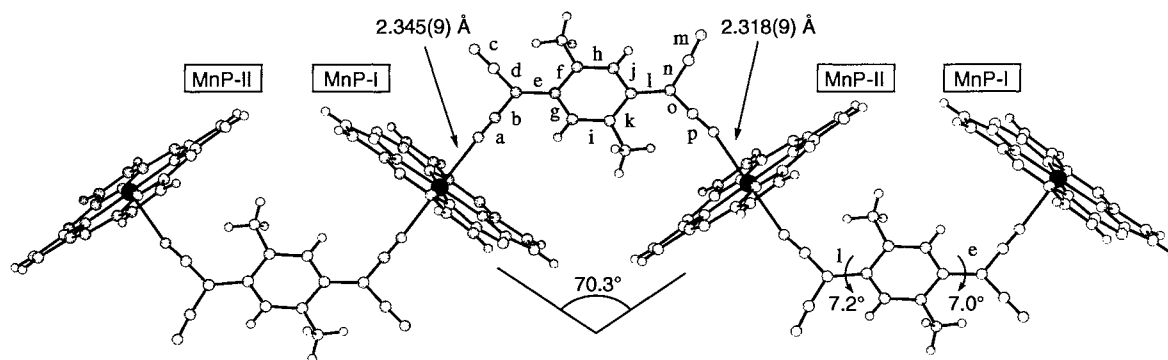
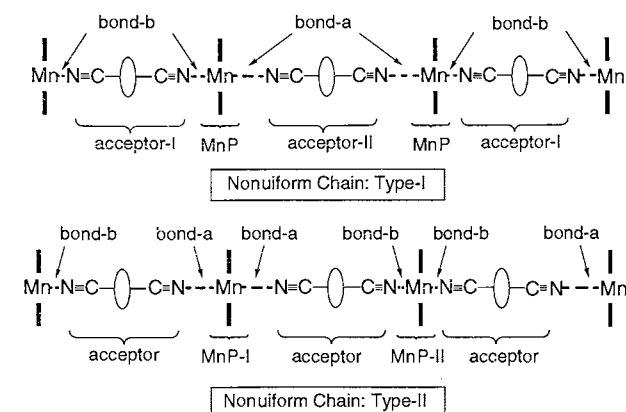


Figure 2. A segment of the 1-D chain structure. For clarity, solvent molecules and aryl groups of [2b]⁺ were omitted. Only Mn^{III} is located on the inversion center of $P\bar{1}$ space group. Intramolecular bond distances of [1b]^{-•} are the followings; a: 1.14, b: 1.44, c: 1.14, d: 1.39, e: 1.43, 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 [MnP][acceptor] having nonuniform chain structures, Type-I and Type-II.

	Type	bond-a (Å)	bond-b (Å)	Δ^a (Å)	θ (K)	T_c (K)	Ref.
[MnOEP][TCNE] ^b	I	2.52	2.36	0.16	5	c)	10
β -[MnPc][TCNE] ^b	I	2.42	2.34	0.08	12	c)	11
β -[MnTF ₄ OMePP][TCNE] ^b	II	2.28	2.29	0.01	93	10.3	12
[2b][1b]	II	2.35	2.32	0.03	23	2.3	d)

^a Δ (Å) = [bond-a] - [bond-b]. ^b OEP: octaethylporphyrinato, Pc: phthalocyanato, TF₄OMePP: *meso*-tetrakis(2,3,5,6-tetrafluoro-4-methoxyphenyl)porphyrinato. ^c Paramagnetic behaviour, not magnetically ordered. ^d 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,^{10,11} 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.¹² The 1-D [2b][1b] chain is nonuniform and is classified into Type-II, as unlike most [MnP][TCNE] complexes.^{1,2} The Mn-N_{1b} distances are 2.345(9) and 2.318(9) Å.¹³ The dihedral angles between [1b]•• and porphyrin planes are 56.8° and 49.0° for MnP-I...[1b]•• and MnP-II...[1b]••, 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 [MnP] salts,¹⁴ but different from the parallel alignment of [MnP][TCNE].^{1,2}

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). 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^{III} and $S = 1/2$ of [1b]•• systems. A minimum in $\chi(T)$ 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 [MnP] ET salts having uniform chain structures are now in

progress.

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- Complex formation reactions were carried out in a glove box with less than 1 ppm oxygen. A filtered hot solution of **2a**⁵ (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 C₁₀₂H₁₀₀MnN₈: C, 80.66; H, 6.30; N, 8.75%. Found: C, 80.38, H, 6.11; N, 8.99%.
- The spectrometers were calibrated so that the Au4f_{7/2} peak of the clean sputtered metals appeared at 84.0 eV. IPs are reproducible to a precision of ± 0.10 eV. Cls = 284.8, N1s = 399.0 Mn2p_{3/2} = 642.8 and Mn2p_{1/2} = 654.6 eV.
- K.-i. Sugiura, S. Mikami, K. Iwasaki, S. Hino, E. Asato, and Y. Sakata, *J. Org. Chem.*, **1999**, submitted; for hexacoordinated Mn^{III} salt ([Mn^{III}TPP][TCNE]): Mn2p_{3/2} = 642.6 and Mn2p_{1/2} = 654.2 eV, for pentacoordinated Mn^{III} salt ([Mn^{III}TPP]Cl): 642.2 and 653.8 eV, for pentacoordinated Mn^{II} salt ([Mn^{II}TPP][pyridine]): 641.1 and 653.1 eV.
- Crystal data for C₈₆H₈₀MnN₈ {[2b][1b]•2*p*-Xylene}, Z = 2, M = 1280.57, triclinic P1 (#2) space group: *a* = 15.460(5) Å, *b* = 16.781(7) Å, *c* = 15.429(6) Å, α = 115.28(3)°, β = 90.876(31)°, γ = 90.881(33)°, *V* = 3618(2) Å³, ρ_c = 1.175 g cm⁻³, λ = 0.71070 Å, *T* = -65 ± 1 °C, $2\theta_{max}$ = 50.0°, *R* (*w*) = 0.076 (0.093), Goodness-of-Fit = 1.38, reflection-parameter ratio = 5.37 based on 4618 unique reflections with *I* > 3 σ (*I*). Data were collected on a Rigaku AFC5R four circled diffractometer system with a graphite monochromated Mo-K α radiation (50 KV X 200 mA) and the structure was solved by a teXSan crystallographic software package from Rigaku.
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