Isolation and Molecular Structure of 1,1,2,4,5,5-Hexacyano-1,4-pentadienyl Anion. An Unusual Reaction of Tetracyanoethylene with *p*-Xylene Mediated by a Porphyrinatomanganese(II)

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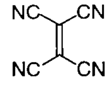
The reaction of TCNE and *meso*-tetrakis(4-biphenylyl) porphyrinatomanganese(II) in *p*-xylene leads to the formation of the 1,1,2,4,5,5-hexacyano-3-(4'-methyphenyl)-1,4-pentadienyl anion, which was characterized by single crystal X-ray diffraction.

Recently, electron transfer complexes constructed from transition metals and cyano-substituted acceptors are being studied due to variety effects arising from cooperative d-π electron interactions.[1] Although tetracyanoethylene (TCNE) **1** is one of the most important component molecules of this research field, the reactive character of its radical anion sometimes produces unexpected products,[2] *i.e.*, $[C_3(CN)_5]^-$,[3] $[(CN)_2C{=}C(CN)O]^-$,[4] *etc.* In the course of our studies on the structure-function relationship for porphyrinatomanganese(III) tetracyanoethenide ([MnP][TCNE]), molecule based magnet,[5-7] we found a new reaction of TCNE with *p*-xylene in the presence of *meso*-tetrakis(4-biphenylyl)porphyrinatomanganese(II), (Mn(II)TBpP) **3**. In this communication, we wish to report the isolation and the molecular structure of 1,1,2,4,5,5-hexacyano-3-(4'-methyphenyl)-1,4-pentadienyl anion **2**.[8]



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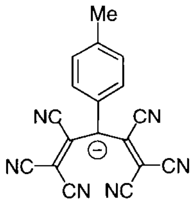

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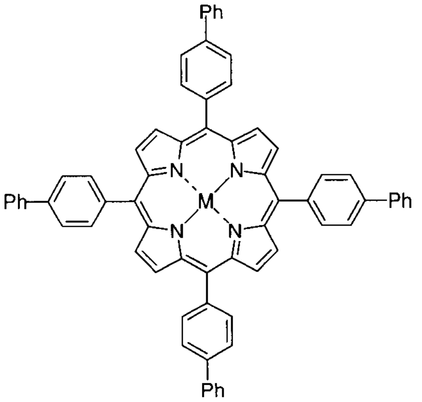

3 (M = Mn(II))

The manganese(II) complex **3** was prepared from the corresponding free base[9] according to the method previously reported.[10,11] The direct redox reaction between TCNE and **3** in *p*-xylene was performed under an inert atmosphere in a glove box keeping oxygen concentration less than 1 ppm. After standing at room temperature for three days under dark conditions, relatively thick (α-crystal) and thin (β) black plates were obtained.[12] The ν_{CN} absorptions at 2194, 2131, and 2126 cm^{-1} for the β-crystals indicate that the crystal is an electron-transfer complex of the ionized component molecules with μ_2-coordination bond as usually seen for [MnP][TCNE].[6] In contrast, the strong absorption at 2205 cm^{-1} and the 2235 and 2180 cm^{-1} weaker absorptions (Figure 1) for the α-crystal suggest the presence of a new chemical species.[13] The negative charge of fast atom bombardment mass spectroscopy analysis of α-crystal showed the presence of an anion having molecular mass $M^- = 307$.

The structure of α was determined to be **2** (Figure 2 and 3) from single crystal X-ray diffraction.[14] The UV-vis. spectrum of α-crystal is nearly identical with that of Mn(III)TBpP chloride, hence the charge of **2** is -1. This anion has C_2 axis through C(39)-C(38)-C(35)-C(40). The benzylic carbon C(40) takes a triangular planer three coordination state with C(35), C(41), and

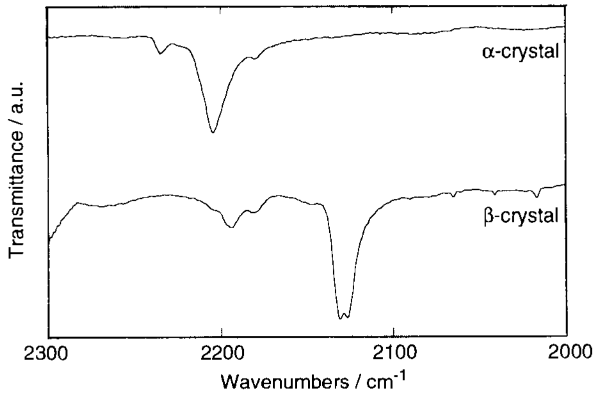

Figure 1. ν_{CN} absorptions of α- and β-crystals (nujol).

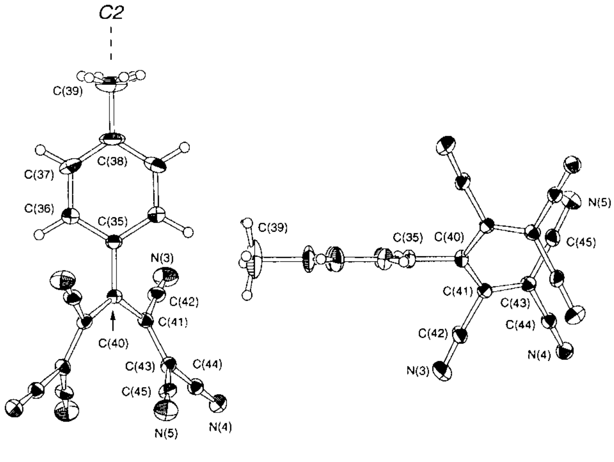

Figure 2. ORTEP drawing of **2**. Thermal ellipsoids are at the 30% probability level. The crystallographyically unique atoms are labeled.

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C(41*). Bond lengths and angles are the followings; C(35)-C(40): 1.476(6) Å, C(40)-C(41): 1.418(4) Å, C(35)-C(40)-C(41): 118.5(2)°, and C(41)-C(40)-C(41*): 123.1(4)°. Steric constraint prevents the two groups of the phenyl and two -C(CN)=C(CN)$_2$ from being coplanar, but forms a propeller. The phenyl ring and -C(CN)=C(CN)$_2$ moieties are at angles of 45.6° and 32.5° to the C(35)-C(40)-C(41)-C(41*) plane. These geometries are similar to the reported values for benzylic carbanions.[15] The bond length of C(41)-C(43) (1.393(4) Å) is longer than that of neutral TCNE (1.344(3) Å)[16] and comparable to that of TCNE anion radical (1.392(9) Å).[3] This result strongly indicates that the anion charge delocalizes over the pentadienyl moiety. The anion coordinates to the Mn(III) at the terminal nitrogen atom N(4) (2.323(3) Å) and produces uniform one-dimensional chain structure (Figure 3). The inter-porphyrin dihedral angle in the chain is 46.0°. This alignment is different from parallel stacked structure for [MnP][TCNE].[5-7]

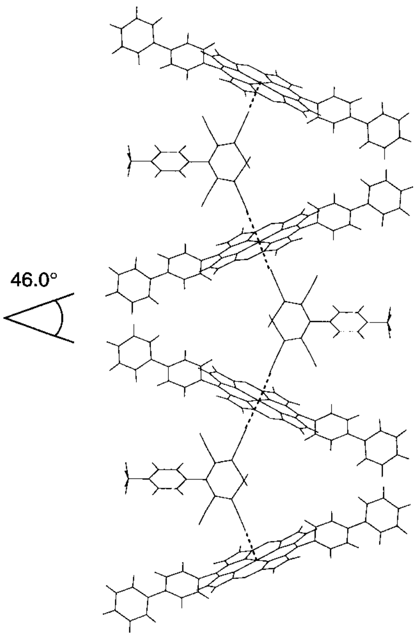

Figure 3. Segment of the 1-D uniform chain structure. For clarity, solvent molecules, front and behind biphenylyl groups of Mn(III)TBpP were omitted. N(4)-Mn(1) coordination bonds, 2.323(3) Å, are indicated by dotted lines.

Since methylated benzenes are commonly used for recrystallization solvents for [MnP][TCNE] formations,[5,6] it is not clear why 3 produces 2 with reproducibility. Our findings will be applied to the preparation of the advanced material based on cyano-substituted acceptors.

We appreciate Professor Joel S. Miller, University of Utah, for helpful discussions.

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11 UV-vis. for **3** (pyridine): 618, 578, and 443 nm.

12 A filtered hot solution of Mn(II)TBpP pyridine complex (5.0 mg, 4.8 μmol) dissolved in 5.0 mL of boiling *p*-xylene was added to TCNE (2.4 mg, 18.7 μmol, 3.9 eq.) dissolved in 5.0 mL of hot *p*-xylene. After standing for three days, the black crystals which formed were harvested by vacuum filtration and dried under vacuum for overnight, 1.5 mg. The product ratio of α- and β-crystal estimated by IR spectroscopy was about 1:1. Both crystals are easily separated by their appearances: mp of α-crystal ~100°C dec.

13 The corresponding values for neutral TCNE: 2259(s) and 2221(m) cm^{-1}; π-anion radical: 2183(s) and 2144(s) cm^{-1}; π-dianion: 2104(s) and 2069(s) cm^{-1}; μ_2-dianion: 2176(m) and 2097(s) cm^{-1}; G. T. Yee, J. C. Calabrese, C. Vazquez, and J. S. Miller, *Inorg. Chem.*, **32**, 377 (1993).

14 Crystal data for [Mn(III)TBpP][**2**][*p*-xylene]$_2$: $C_{102}H_{71}MnN_{10}$, FW = 1491.69, monoclinic, C2/c (#15), 0.63 X 0.53 X 0.05 mm^3, -70.1±1.0 °C, Mo-K$_\alpha$, a = 37.313(3), b = 11.592(4), c = 23.698(4) Å, β = 129.230(7)°, V = 7939(2) Å^3, Z = 4, R = 0.055, Rw = 0.055 for 4221 independent reflections (I>3.00σ(I)). The bond lengths of **2** are the followings; C(35)-C(36): 1.393(4), C(35)-C(40): 1.476(6), C(36)-C(37): 1.368(5), C(37)-C(38): 1.376(5), C(38)-C(39): 1.512(9), C(40)-C(41): 1.418(4), C(41)-C(42): 1.443(4), C(41)-C(43): 1.393(4), C(43)-C(44) 1.421(4), C(43)-C(45): 1.420(4), N(3)-C(42): 1.140(4), N(4)-C(44): 1.146(4), and N(5)-C(45): 1.140(4) Å.

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