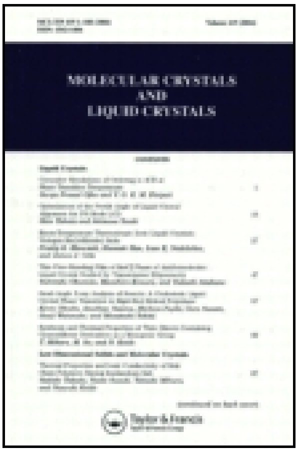

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Reactions of Mn(III) Quadridentate Schiff Base Compounds with TCNQ Anion to Form Unusual TCNQ Derivatives by Alcoholysis

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Reactions of Mn(III) Quadridentate Schiff Base Compounds with TCNQ Anion to Form Unusual TCNQ Derivatives by Alcoholysis

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The reactions of Mn(III) quadridentate Schiff base compounds, [Mn(saltmen)(H_2O)]ClO_4 (**1**; saltmen^{2-} = *N*, *N'*-(1, 1, 2, 2-tetramethylethylene)bis(salicylideneiminato)) and [Mn(naphtmen)(H_2O)]ClO_4 (**2**; naphtmen^{2-} = *N*, *N'*-(1, 1, 2, 2-tetramethylethylene)bis(naphthylideneiminato)), with LiTCNQ gave three type compounds according to reaction conditions: [Mn(saltmen)(H_2O)](TCNQ) (**3**), [Mn(saltmen)(MeOH)(TCNQ-OMe)] (**4**, TCNQ-OMe$^-$ = *p*-(α,α-dicyano-α-methoxytolyl)dicyanomethide), and [Mn(naphtmen)(MeOH)(TCNQA-OMe)] (**5**, TCNQA-OMe$^-$ = *p*-(α-cyano-α-methoxy-α-methylamidetolyl)dicyanomethide).
Compounds **3** and **4** are distinguishable according to synthetic condition either anaerobic or not. Compound **5** is synthesized in aerobic condition as well as **4**. For **4** and **5**, unusual addition reactions on the anionic TCNQ molecule occur to form (TCNQ-OMe)$^-$ for **4** and (TCNQA-OMe)$^-$ for **5**.

Keywords: Mn(III) quadridentate Schiff base compounds; TCNQ derivatives; assembly reactions; addition reactions

INTRODUCTION

Since the pioneering research for tetracyanoethane (TCNE) and tetracyanoquinodimethane (TCNQ) at Dupont in the 1950s and 1960s[1], the research of polycyano organic molecules and their derivatives is continuing in the field of molecule-based materials, owing to the utility as an electron acceptor of polycyano organic molecules to produce the electron-conjugated systems and electron-transfer systems. The TCNQ and TCNE molecules often bring about some addition reactions and substitution reactions itself when they assemble to metal ions or metal complexes[2]. The radical anion of TCNQ self aggregates to form the σ-bonded dimer $[TCNQ\text{-}TCNQ]^{2-}$, namely of which reaction is known as homo-radical coupling, and the structure was revealed by searching of its metal-assemblies[2]. As supposed from the formation of σ-bonded dimer $[TCNQ\text{-}TCNQ]^{2-}$, the methylene moiety of neutral TCNQ and TCNQ anion is an active site on some addition reactions and the radical coupling. The hydrolysis of TCNQ and TCNE is one of the well-known reactions, producing α,α-dicyano-*p*-toluoylcyanide[3] and tricyanoethenolate[4], respectively. During our searching on the assembly reaction of Mn(III) salen analogues with TCNQ anion, unique addition reactions of TCNQ anion were revealed: the reaction of $[Mn(saltmen)(H_2O)]ClO_4$ (**1**, $saltmen^{2-}$ = *N*, *N'*-(1, 1, 2, 2-tetramethylethylene)bis(salicylideneiminato) dianion) with $Li^+TCNQ^{\cdot-}$ affords the continuous formation of $[Mn(saltmen)(H_2O)](TCNQ)$ (**3**) and [Mn(saltmen)(MeOH)(TCNQ-OMe)] (**4**, $TCNQ\text{-}OMe^-$ = *p*-(α,α-dicyano-α-methoxytolyl)dicyanomethide) in methanol/water mixture. On the other hand, the reaction of $[Mn(naphtmen)(H_2O)]ClO_4$ (**2**, $naphtmen^{2-}$ = *N*, *N'*-(1, 1, 2, 2-tetramethylethylene)bis(naphthylideneiminato) dianion) affords [Mn(naphtmen)(MeOH)(TCNQA-OMe)] (**5**, $TCNQA\text{-}OMe^-$ = *p*-(α-cyano-α-methoxy-α-methylamidetolyl)dicyanomethide). Here the syntheses, structures and magnetic properties of these assemblies **3** – **5** are described.

EXPERIMENTAL DATA

Anal. Calcd for $[Mn(saltmen)(H_2O)](TCNQ)$ (**3**), $C_{32}H_{28}N_6O_3Mn$: C, 64.11; H, 4.71; N, 14.02. Found: C, 63.65; H, 4.91; N, 14.46. IR on KBr: ν (C≡N), 2195, 2183, 2152, 2135; ν (C=N; Schiff base imine), 1603 cm^{-1}. *Crystal data:* **3**·MeOH: $C_{33}H_{32}N_6O_4Mn$, M = 631.59, triclinic, a =

8.6270(5), b = 13.025(1), c = 14.185(1) Å, α = 87.695(1) °, β = 88.869(3) °, γ = 72.075(5) °, U = 1515.3(2) Å^3, T = -170 °C, space group P-1 (no. 2), Z = 2, μ(Mo-Kα) = 4.84 cm^{-1}, 14414 reflections measured, 6888 unique (R_{int} = 0.048), refinement method: full-matrix least-squares on F^2. The final R indices: R_1 = 0.052 ($I > 2\sigma(I)$), R = 0.088, wR = 0.147 (all data), GOF = 1.00.

Anal. Calcd for [Mn(saltmen)(MeOH)(TCNQ-OMe)] (**4**), $C_{34}H_{33}N_6O_4Mn$: C, 63.35; H, 5.16; N, 13.04. Found: C, 63.21; H, 4.89; N, 13.38. IR on KBr: ν (C≡N), 2187, 2124; ν (C=N; Schiff base imine), 1605 cm^{-1}.

Anal. Calcd for [Mn(naphtmen)(MeOH)(TCNQA-OMe)] (**5**), $C_{43}H_{41}N_6O_5Mn$: C, 66.49; H, 5.32; N, 10.82. Found: C, 66.31; H, 5.30; N, 11.28. IR on KBr: ν (N-H), 3301; ν (C≡N), 2181, 2124; ν (C=O; secondary amide), 1670; ν (C=N; Schiff base imine), 1618, 1599, 1583 cm^{-1}. *Crystal data:* **5**: $C_{43}H_{41}N_6O_5Mn$, M = 776.77, monoclinic, a = 13.8790(6), b = 13.9535(6), c = 19.9537(7) Å, β = 97.814(1) °, U = 3828.4(3) Å^3, T = -150 °C, space group $P2_1/c$ (no. 14), Z = 4, μ(Mo-Kα) = 3.99 cm^{-1}, 29935 reflections measured, 8733 unique (R_{int} = 0.075), refinement method: full-matrix least-squares on F^2. The final R indices: R_1 = 0.060 ($I > 3\sigma(I)$), R = 0.090, wR = 0.134 ($I > 3\sigma(I)$), GOF = 1.42.

RESULTS AND DISCUSSION

Syntheses and Characterizations

Compound **3** was synthesized by the assembly reaction of **1** and LiTCNQ in a degassed methanol/water mixture, while compound **4** was derived from a similar reaction in aerobic condition. IR spectra clearly indicate the differences between these compounds. Especially, the ν (C≡N) modes are strongly affected by the redox-state, the structural feature of TCNQ derivatives, and the nature of metal-binding interaction. For **3**, four ν (C≡N) stretches at 2195, 2183, 2152, and 2135 cm^{-1} are observed, which are lower energies than free neutral TCNQ (2222 cm^{-1}), being due to the TCNQ anionic form. On the other hand, for **4**, two ν (C≡N) stretches at 2187 and 2124 cm^{-1} are detected as sharp strong modes. The latter one is considerably lower value, which thus indicates that it is contributed from TCNQ derivatives different from both the neutral and anionic TCNQs.

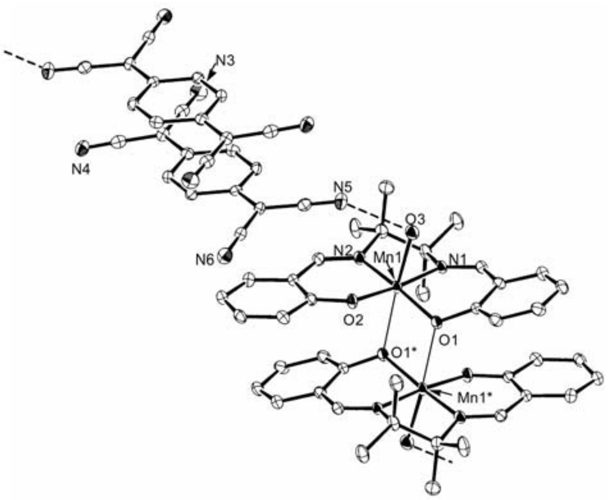

FIGURE 1 ORTEP drawing of **3**. The dashed line expresses the inter-molecular hydrogen bonds.

Compound **5** was obtained in the reaction of **2** with LiTCNQ in aerobic condition as well as **4**. The ν (C≡N) mode has the same pattern (two stretches at 2181 and 2124 cm^{-1}) as **4**. Additionally, the ν (C=O) stretch of secondary amide group is newly detected at 1670 cm^{-1}. These IR data support the structural data on X-ray analyses.

Structural Descriptions

Compound **3** was structurally characterized by single-crystal X-ray crystallography. ORTEP drawing is depicted in Figure 1. $[Mn(saltmen)(H_2O)]^+$ and $TCNQ^-$ groups situate separately and form own dimerizarion, where the former makes a out-of-plane dimer bridged by phenalote oxygens. The characteristic bond distances and angles in the part of the out-of-plane dimeric core are: Mn···Mn* = 3.3183(8) Å, Mn-O(1) (O(1) : intramolecular phenolate oxygen) = 1.901(2) Å, Mn-O(1)* (O(1)*: intermolecular phenolate oxygen) = 2.431(2) Å, Mn-O(1)*-Mn* = 99.27(7) °, O(1)-Mn-O(1)* = 80.73(7) ° (*; 1-x, -y, 2-z). The apical positions of the Mn(III) ion are occupied by a phenolate oxygen atom, O(1)*, of the neighboring $[Mn(saltmen)(H_2O)]^+$ unit and a water oxygen atom, O(3), with Mn-O(3) = 2.204(2) Å, assuming a distorted square bipyramidal coordination geometry due to the Jahn-Teller elongation (equatorial Mn-X bond distances: av. Mn-O = 1.885(2) Å; av. Mn-N = 1.983(2) Å). The anionic TCNQ group makes stacking motif with the

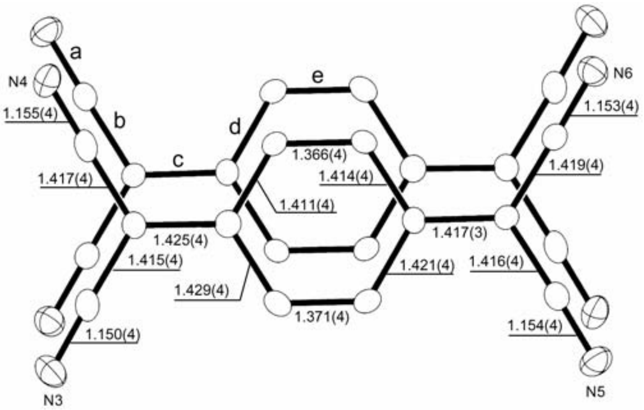

FIGURE 2 The dimerized TCNQ⁻ groups in **3** with the bond distances and the bond descriptions (a – e) used in the relationship $\rho = A[c/(b + d)] + B$ (A = -41.667 and B = 19.833 (see text).

plane-to-plane distance of ca. 3.1 Å. The bond distances in TCNQ moiety are important to estimate its redox-state. The correlation between the constituent bond distances and redox-state in TCNQ has been derived by Kistenmacher et al. using the relationship $\rho = A[c/(b + d)] + B$ (A = -41.667 and B = 19.833 are determined from neutral TCNQ ($\rho = 0$)[5] and RhTCNQ (ρ = -1) [6]) [7]. The values of b, c, and d are constituent distances in TCNQ defined in Figure 2. The estimated ρ value for **3** is found to be –1.1. These structural data and IR data prove the presence of the monoanionic form of TCNQ. The inter-molecular hydrogen bond is presented between water oxygen O(3) in $[Mn(saltmen)(H_2O)]^+$ unit and N(5) in TCNQ- moiety with the distance of O(3)···N(5) = 2.793(3) Å (dashed line in Figure 1).

The crystal structure of **5** was revealed as shown in Figure 3a. Compound **5** is a mono-Mn(III) species with naphtmen^{2-} quadridentate ligand (equatorial Mn-X bond distances: av. Mn-O = 1.887(4) Å; av. Mn-N = 1.974(4) Å). The apical positions are occupied by methanol and *p*-(α-cyano-α-methoxy-α-methylamidetolyl)dicyanomethide (TCNQA-OMe⁻) with the bond distances of Mn-O(5) = 2.283(4) Å and Mn-N(3) = 2.267(5) Å, thus taking a distorted square bipyramidal coordination geometry with the Jahn-Teller elongation. The discrete molecules are connected by a inter-molecular hydrogen bond with O(5)···N(4) = 2.752(7) Å, forming hydrogen-bonded 1-D chain arrangement.

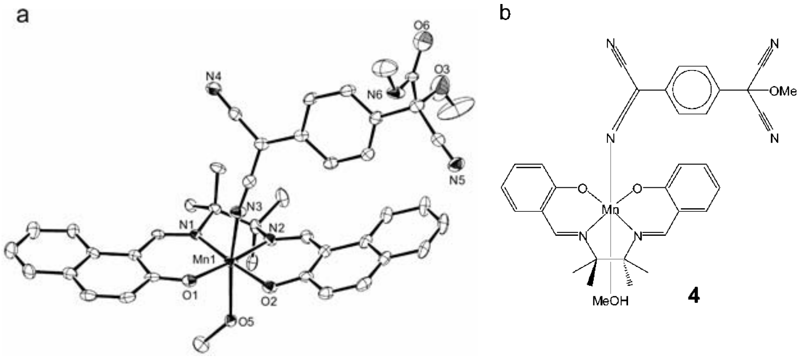

FIGURE 3 ORTEP drawing of **5** (a) and the presumed structure of **4** (b).

The structural data of **5** support the presumed structure of **4** (Figure 3b). Additionally, the ν (C≡N) mode in IR spectrum for **4** are the almost same as that for **5**. Consequently, the TCNQ derivative containing in **4** should be *p*-(α, α-dicyano-α-methoxytolyl)dicyanomethide (TCNQ-OMe^{-}).

Magnetic Properties

Temperature-dependence of the magnetic susceptibility of **3** - **5** was measured on the ground polycrystalline samples in the temperature range from 2.0 to 300 K under 1 T. The magnetic behavior of **3** is unusually shown (Figure 4; the $\chi_m T$ vs T plot of **3**), while those of **4** and **5** are completely demonstrated as a paramagnetic $S = 2$ spin ground state. For **3**, the $\chi_m T$ value at 300 K is found to be 3.20 cm^3·K·mol^{-1}, which suggests composing of a summation of $S = 2$ arising from Mn(III) ion and $S = 1/2$ arising from TCNQ^{-}. Upon cooling, the $\chi_m T$ value continuously decreases to reach the minimum at 84 K (3.01 cm^3·K·mol^{-1}), and then slightly increases to 3.08 cm^3·K·mol^{-1} at 44 K. This behavior should be due to co-existence of antiferromagnetic interaction in the TCNQ^{-} stacking dimer and ferromagnetic interaction in the out-of-plane dimer $[Mn_2(saltmen)_2(H_2O)_2]^{2+}$. The ferromagnetic interaction in the Mn(III) out-of-plane dimers is not unusual as demonstrated in the similar compounds reported previously[8]. The decrease at low temperature could be associated with principally two phenomena, the zero-field splitting (ZFS) arising from Mn(III) ion and/or possible inter-molecular antiferromagnetic interaction, probably between the out-of-palne dimer units via TCNQ^{-} dimer units.

For **4** and **5**, the $\chi_m T$ value at 300 K is found to be 278 and 3.01

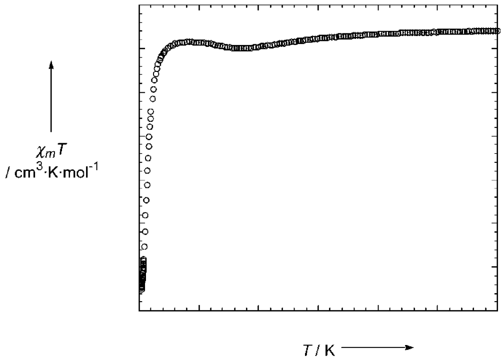

FIGURE 4 Temperature-dependence of $\chi_m T$ of **3**.

$cm^3 \cdot K \cdot mol^{-1}$, respectively. The $\chi_m T$ is almost linear between 50 and 300 K in both compounds, showing paramagnetic behavior based on $S = 2$ from Mn(III) ion. Then, it decreases in the low temperature region (1.41 $cm^3 \cdot K \cdot mol^{-1}$ for **4** and 1.67 $cm^3 \cdot K \cdot mol^{-1}$ for **5** at 2.0 K) by influences of ZFS and/or inter-molecular antiferromagnetic interaction. The best-fitting parameters including ZFS term (D) and inter-molecular interaction (zJ) are $g = 1.94$, $D = -0.22$ cm^{-1}, and $zJ = -0.38$ cm^{-1} for **4** and $g = 2.01$, $D = -1.73$ cm^{-1}, and $zJ = -0.16$ cm^{-1} for **5**, which are reasonable values for typical Mn(III) quadridentate Schiff base compounds[8,9].

SUMMARY

Here, three unique compounds consisting of Mn(III) salen analogues and TCNQ derivatives were fully characterized. The alcoholysis reactions described here were not provided without the presentation of Mn(III) salen analogues, **1** or **2**. Further investigations used other Mn(III) salen analogues may open new TCNQ chemistry.

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