Unprecedented Two-Dimensional Polymers of Mn(II) with TCNQ$^{-•}$ (TCNQ = 7,7,8,8-Tetracyanoquinodimethane)

Hanhua Zhao, Robert A. Heintz, and Kim R. Dunbar*

Department of Chemistry and the Center
for Fundamental Materials Research
Michigan State University
East Lansing, Michigan 48824

Robin D. Rogers

Department of Chemistry, The University of Alabama
Tuscaloosa, Alabama 35487

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The concept of combining in one "hybrid" the special properties of individual inorganic and organic components is a topic of major interest in the materials community.[1] In one approach, researchers are coassembling transition metal spin centers and organonitrile radicals into covalent networks,[2,3] efforts that have unearthed extraordinary materials including highly metallic polymers of Cu with DCNQI (DCNQI = *N*,*N*′-dicyanoquinonediimine),[4] an electrically bistable material of Cu with TCNQ (TCNQ = 7,7,8,8-tetracyanoquinodimethane),[5] and a bulk ferromagnet of V with TCNE (TCNE = tetracyanoethylene).[6] With the exception of the DCNQI systems, however, X-ray structures of these intriguing compounds have not been obtained. Clearly, the main obstacle to be overcome in this chemistry is rapid precipitation of the products, which are typically far too insoluble to allow for recrystallization.

As part of our investigation into the use of homoleptic acetonitrile cations as precursors for new materials, we discovered that the compounds $[M(CH_3CN)_6][BF_4]_2$ (M = Fe, Mn, Co, and Ni) react with 2 equiv of $[^nBu_4N][TCNQ]$ in CH_3CN to yield microcrystalline products.[7] While attempting to grow single crystals of the Mn compound, it was found that two entirely different products are formed in the presence of MeOH. Herein we report the X-ray structures, infrared spectra, and magnetism of two novel metallopolymers in which manganese ions are involved in unprecedented arrangements with ligands derived from $[TCNQ]^{-•}$.

Rapid mixing of methanolic solutions of $[Mn(MeCN)_4][BF_4]_2$ and $[^nBu_4N][TCNQ]$ instantaneously yields a purple microcrystalline solid formulated as $Mn(TCNQ)_2(MeOH)_2$.[8] Slow diffusion of the parent compounds in MeOH leads to blue triclinic parallelepipeds of $[Mn(TCNQ{-}TCNQ)(MeOH)_2{\cdot}MeOH]_\infty$ **(1)** (TCNQ−TCNQ = σ-dimerized $[TCNQ]^{-•}$) are formed.[9a] A crystallographic study revealed that **1** is composed of a 2-D network of six-coordinate Mn(II) ions equatorially bound to the four outer nitrile groups of the unusual $[TCNQ{-}TCNQ]^{2-}$ ligand (Figure 1). The tetradentate dianion is nonplanar which leads to a staircase motif, with each "step" consisting of infinite chains of Mn(II) ions joined by 12-membered metallacyclic rings involving *cis*-nitriles that lie in the same plane. A labeled diagram of a portion of **1** is given in Figure 2a, and a packing diagram of the layers is depicted in Figure 2b. The novel 2-D structure is stabilized by extensive interlayer hydrogen bonding that involves axial MeOH ligands and interstitial MeOH molecules situated between the layers (linear O1···O2 = 2.629 Å and bent O1···O2′ = 2.983 Å).

Purple monoclinic needles of $[Mn(TCNQ)(TCNQ{-}TCNQ)_{0.5}(MeOH)_2]_\infty$ **(2)** are formed by slow diffusion of the reactants in a MeOH/MeCN mixture.[10a] Crystals of **2** also exhibit a 2-D structure, but in this case the Mn(II) centers are coordinated to tetradentate $[TCNQ{-}TCNQ]^{2-}$ and bidentate $[TCNQ]^{-•}$ ligands (Figure 3a); the latter act as bridging ligands through the 1,2-dicyano positions with the two unligated N≡C- groups pointing outward from the edges of the zig-zag layers towards axial MeOH ligands in the adjacent layers (N3···O2A = 2.834 (8) Å and N4···O1A = 2.846 (8) Å). These hydrogen bonds serve to stabilize a densely packed, interdigitated arrangement of layers as shown in Figure 3b.

The importance of the current X-ray structures lies in the fact that they are only the second and third crystallographically determined binary materials of TCNQ since their discovery in 1962.[11a] Prior to the present results, the only related structurally characterized example is $[Ag(\mu_4\text{-}TCNQ)]_\infty$, which consists of tetrahedral Ag(I) ions bridged by spiral columns of μ_4-$[TCNQ]^{-•}$ groups that stack at ~3.5 Å along the *a* axis.[12a] There are several known complexes of Mn(II) with TCNQ behaving as a ligand,[13,14] but the only extended structure is a 1-D polymer of Mn with $[TCNQ]^{2-}$ bridges and Schiff base coligands.[12b] To our knowledge, however, there are no structures of coordination compounds with $[TCNQ{-}TCNQ]^{2-}$ ligands. In fact, that $[TCNQ{-}TCNQ]^{2-}$ entity has only been documented three previous times and in these instances it behaves as an outer-sphere anion.[14] The C−C bonds of 1.659(10) and 1.635(10) Å (f−f′ in Figure 1) that join the $[TCNQ]^{-•}$ units in **1** and **2** are long, but obviously significant since the C atoms involved are

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[7] The products, formulated as $M(TCNQ)_{1.5}$, undergo a transition to a bulk ferromagnet at $T \le 50$ K. A powder pattern of the Ni product indexed as $a = 12.108$ Å, $b = 12.108$ Å, $c = 8.537$ Å, $\alpha = \beta = \gamma = 90°$, $V = 1251$ Å^3 for $F_{20} = 19$.

[8] Anal. ($C_{26}H_{16}N_8O_2Mn$) Calcd: C, 59.21; H, 3.06; N, 21.24. Found: C, 59.53; H, 2.41; N, 21.71.

[9] Crystal data for **(1)**: $C_{28}H_{24}N_8O_4Mn$, FW = 591.49, blue parallelepipeds, triclinic, *P*-1, $a = 7.2966$ (8) Å, $b = 7.4289(8)$ Å, $c = 14.060(2)$ Å, $\alpha = 76.112(2)°$, $\beta = 87.242(2)°$, $\gamma = 71.891(2)°$, $V = 702.91(13)$ Å^3, $Z = 1.3 < 2\theta < 46.5$, unique data = 1967, $I > 2\sigma(I) = 1935$. Data were collected on a Siemens SMART CCD area detector at −150(1) °C and solved and refined in SHELXTL v.5.0 by full-matrix least-squares on F^2. Final *R* (Rw) = 6.87 (15.46), goodness-of-fit (GOF) = 1.32 for 1962 data and 198 parameters.

[10] Crystal data for **(2)**: $C_{26}H_{16}N_8O_2Mn$, FW = 527.41, purple needles, monoclinic, *C*2/*c*, $a = 14.4378(5)$ Å, $b = 27.3067(11)$ Å, $c = 13.1238(5)$ Å, $\beta = 90.057(1)°$, $V = 5174.0(3)$ Å^3, $Z = 8$, $3.6 < 2\theta < 52.02°$, unique data = 3724, $I > 2\sigma(I) = 3290$. Data were collected on a Siemens SMART CCD area detector at −100(1) °C and solved and refined in SHELXTL v.5.0 by full-matrix least-squares on F^2. The original cell and absences suggested orthorhombic C-centered, but the structure was ultimately solved as a 50/50 twin in *C*2/*c* (twinning law 100, 010, 00−1). The disordered MeOH group was modeled in two orientations with occupancies 0.45 C(25) and 0.55 C(25′): *R* (Rw) = 6.78 (12.10), GOF = 1.22 for 3712 data and 348 parameters.

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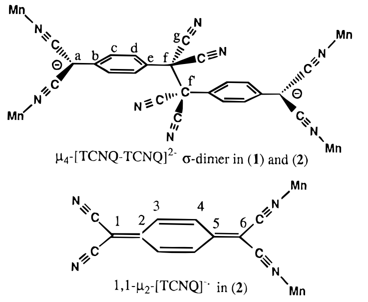

μ4-[TCNQ-TCNQ]$^{2-}$ σ-dimer in (**1**) and (**2**)

1,1-μ2-[TCNQ]$^{-\bullet}$ in (**2**)

	(1)	**(2)**
a-b	1.464(7)	1.459(7)
b-c	1.397[6]	1.39[1]
c-d	1.376[2]	1.385[8]
d-e	1.394[2]	1.38[2]
e-f	1.524(7)	1.528(7)
f-f'	1.659(10)	1.635(10)
f-g	1.479[1]	1.48(2)
1-2		1.404(8)
2-3		1.43[2]
3-4		1.356[8]
4-5		1.43[1]
5-6		1.421(7)

Figure 1. Schematic of the [TCNQ−TCNQ]$^{2-}$ and 1,1-μ^2-[TCNQ]$^{-\bullet}$ ligands and key distances for **1** and **2**.

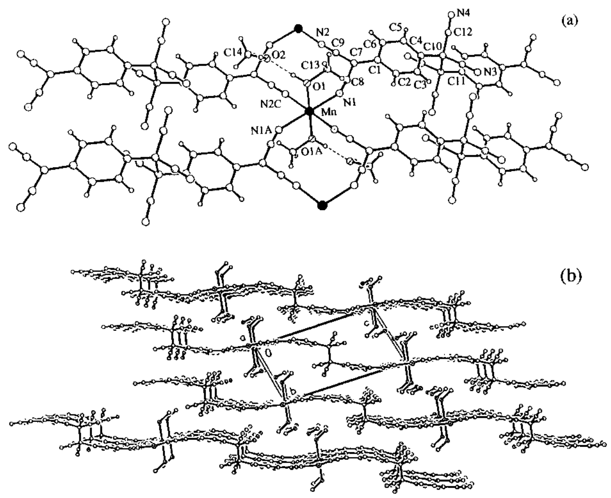

Figure 2. (a) PLUTO diagram of a portion of **1** with important bond distances (Å) and angles (deg) as follows: Mn−O1, 2.172(4); Mn−N1, 2.219(4); N1−C8, 1.148(6); C1−C7, 1.464(7); C10−C10′, 1.659(10); O1−Mn−O1, 180; C4−C10−C12, 111.4(40; C4−C10−C10′, 111.8(5); C4−C10−C11, 112.0(4). (b) Packing diagram of the layers viewed in the *bc* plane.

essentially tetrahedral. The similarity of all the distances in the rings and the significant lengthening of the C═C bond in the planar exocyclic C═C(CN)$_2$ groups support the aromatic resonance structure for [TCNQ−TCNQ]$^{2-}$ depicted in Figure 1.[2] The corresponding metric parameters for the 1,1-μ_2-[TCNQ]$^{-\bullet}$ ligand in **2** are in accord with data reported for other structures containing [TCNQ]$^{-\bullet}$.[2,15]

The position of the ν(C≡N) modes is useful for assigning charge as well as predicting stacking modes in TCNQ^{n-} salts.[2,16] IR data for metal-bound TCNQ ligands are complicated by the fact that ν(C≡N) stretches can shift to higher energies if the TCNQ acts primarily as a σ-donor or to lower energies if there is significant metal to TCNQ π-backbonding. As an alternative, the δ(C−H) mode was examined, which proved to bey very useful for detecting the two structural variations of [TCNQ]$^{-\bullet}$ in **1** and **2**.[13e,18,19] The IR spectrum of **1** exhibits a δ(C−H) mode at 806 cm^{-1} in accord with the presence of only [TCNQ−TCNQ]$^{2-}$; whereas, the spectrum of **2** revealed an absorption at 825 cm^{-1} ([TCNQ]$^{-\bullet}$) and 802 cm^{-1} ([TCNQ−TCNQ]$^{2-}$).[17,19] These assignments will prove to be useful for identifying the presence of σ-dimerized [TCNQ]$^{-\bullet}$ in the numerous metal/TCNQ materials for which X-ray data is unavailable.

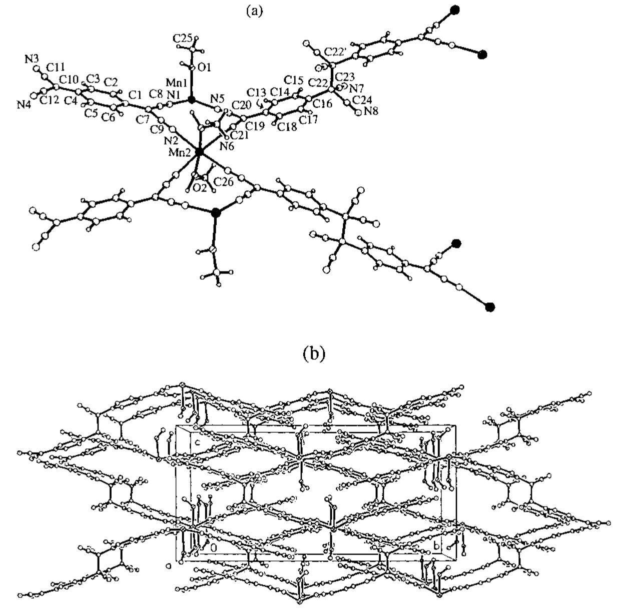

Figure 3. (a) PLUTO diagram of a segment of one zig-zag chain in **2** with important bond distances (Å) and angles (deg) as follows: Mn1−N1, 2.226(6); Mn1−N5, 2.183(6); Mn1−O1, 2.191(5); Mn2−O2, 2.161(5); Mn2−N6, 2.161(6); N1−C8, 1.129(8); N5−C20, 1.151(8); C1−C7, 1.421(7); C2−C3, 1.364(9); C4−C10, 1.404(8); C11−N3, 1.147(9); C13−C19, 1.459(7); C14−C15, 1.393(9); N1−Mn1−N5, 87.9(2); O1−Mn1−O1′, 175.1(3); O2−Mn2−N6, 94.6(2); C4−C10−C11, 122.3(6); C16−C22−C22′, 112.6(5). (b) Extended packing diagram of the layers in **2** viewed in the *bc* plane.

The diamagnetic [TCNQ−TCNQ]$^{2-}$ units serve to magnetically isolate the $S = {}^5/_2$ Mn(II) spin centers, as evidenced by the Curie behavior of **1** between 5 and 300 K ($\mu_{\mathrm{eff}} = \sim 5.9$ BM).[20] Compound **2** exhibits Curie−Weiss behavior over the same temperature range and a higher moment ($\mu_{\mathrm{eff}} = \sim 6.9$ BM), which corresponds to the presence of one [TCNQ]$^{-\bullet}$ radical per Mn(II) ion. Compelling evidence for the importance of the σ-dimerized [TCNQ]$^{-\bullet}$ in preventing magnetic coupling of spins throughout the solid comes from data obtained for a phase prepared from the same starting complexes in MeCN. This compound exhibits a ferromagnetic transition at ~50 K and displays one δ(C−H) bend at 827 cm^{-1} assignable to [TCNQ]$^{-\bullet}$ but no feature near 800 cm^{-1} where the δ(C−H) of [TCNQ−TCNQ]$^{2-}$ has been found to occur (vide supra). Full details of the products of Mn(II) and other 3d metals with [TCNQ]$^{-\bullet}$ in acetonitrile will appear in due course.[21]

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Supporting Information Available: A description of X-ray data collection and refinement, crystal data, atomic coordinates, bond distances and angles, anisotropic displacement parameters, hydrogen coordinates, and ORTEP diagrams for **1** and **2** and spectral and magnetic data (27 pages). See any current masthead page for ordering and Internet access instructions.

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[17] (a) IR data for **(1)** (Nujol, KBr): ν(C≡N), 2202 vs, br, 2139 bs, br cm^{-1}; δ(C−H) 806 m cm^{-1}. (b) IR data for **(2)** (Nujol, KBr): ν(C≡N), 2216 vs, 2187 vs, 2168 s, 2156 s cm^{-1}1; δ(C−H) 825 m, 802 m cm^{-1}.

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[20] Magnetic susceptibility data were collected on a Quantum Design, Model MPMS, superconducting quantum interference device between 5 and 320 K at a field of 1000 G.

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