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Stabilization of Magnetic Ordering Observed for the Bridging NCN Group

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Supporting Information

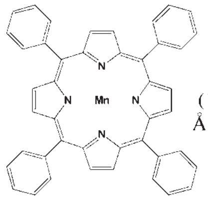
ABSTRACT: The reaction of *meso*-tetraphenylporphyrinatomanganese(II) (MnTPP) and *N*,7,7-tricyanoquinomethanimine (TCQMI) forms $\{[\mathrm{Mn^{III}TPP}]^+\}_2[\mathrm{TCQMI}]_2^{2-}$, which possesses a one-dimensional chain with $\mu_{1,3}$-NCN linkages. The reduced $[\mathrm{TCQMI}]^{\bullet-}$ dimerizes as $[\mathrm{TCQMI}]_2^{2-}$ with a long, central 1.611(8) Å C−C bond and leads to a honeycomb, two-dimensionally layered structure with 24-membered rings. The $\mu_{1,3}$-NCN linkage stabilizes a canted antiferromagnetic (weak ferromagnetic) behavior with T_c of 3.7 K.

Tetraphenylporphyrinatomanganese(III) compounds possessing radical anions that bridge the $S = 2$ $\mathrm{Mn^{III}}$ sites comprise a family of unusual linear-chain-structured organic-based ferrimagnets. They are ferrimagnets with magnetic ordering temperatures (T_c) up to 28 K[1] and have complex history- and temperature-dependent magnetizations that include extraordinarily high coercivities (~27 kOe) at low temperature that exceed commercial magnets.[2]

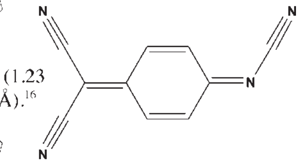
The most studied radical anion is $[\mathrm{TCNE}]^{\bullet-}$ (TCNE = tetracyanoethylene),[3] although substituted 7,7,8,8-tetracyano-*p*-quinodimethanes (TCNQ),[4] and chloranil,[5] etc., also stabilize magnetic ordering. To extend this family of materials, we have investigated the reaction of *meso*-tetraphenylporphyrinatomanganese(II) (MnTPP) and *N*,7,7-tricyanoquinomethanimine (TCQMI).[6]

This reaction[7] forms nonsolvated $[\mathrm{Mn^{III}TPP}][\mathrm{TCQMI}]$. TCQMI was reduced, as evidenced by the ν_{CN} IR (KBr) absorptions being reduced from 2230 and 2169 $\mathrm{cm^{-1}}$ for $\mathrm{TCQMI^0}$ to 2188 and 2106 $\mathrm{cm^{-1}}$. The structure was determined from single-crystal X-ray diffraction[8] and consists of a warped MnTPP with an average Mn−N distance of 2.023 Å and a σ-$[\mathrm{TCQMI}]_2^{2-}$ dimer. $[\mathrm{TCQMI}]_2^{2-}$ dimerizes with a $(\mathrm{NC})_2\mathrm{C}{-}\mathrm{C}(\mathrm{CN})_2$ linkage with a long, central 1.611(8) Å C−C bond (Figure 1). The $\mathrm{Mn^{III}}$ ion lies out of the plane of the four N atoms bound to it. This bond length is in accordance with the bond lengths exhibited by the related σ dimers of $[\mathrm{TCNQ}]^{\bullet-}$ (~1.6 Å)[9] and $[\mathrm{TCNE}]^{\bullet-}$ [1.59(2) Å].[10−14]

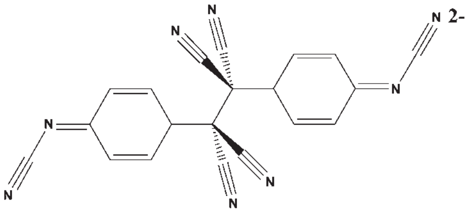
On the opposite side of the dimer, the linear NCN fragment bonds to two $\mathrm{Mn^{III}}$ ions in a $\mu_{1,3}$-bridging manner with 2.382(2) and 2.241(3) Å separations. The NC bond lengths of the NCN fragment [1.318(4) and 1.161(4) Å] indicate a cyanimine (N—C≡N) structure and not a carbodiimide (N=C=N) resonance structure. This is consistent with similar structures seen for a series of $\mathrm{Mn^{III}}$Salen compounds bridged by hydrogencyanamide (HNCN) that exhibit the cyanamide form with two different C−N bonds [1.294(4) and 1.171(4) Å].[15] In contrast, $\mathrm{Mn^{II}NCN}$ possesses the carbodiimide (N=C=N) resonance structure with two equivalent C−N bonds (1.23 Å).[16]



MnTPP



TCQMI



$[\mathrm{TCQMI}]_2^{2-}$

The warped porphyrin rings adopt a staggered orientation, with alternating planes canted. Warping of the porphyrins, particularly of TPP, has been ascribed to the porphyrin shifting to allow more favorable overlap between its orbitals and those of the central metal.[17] This is most likely due to the steric constraints of the dimer. Hence, $\mathrm{Mn^{III}{-}NCN{-}Mn^{III}}$ linkages with 6.204 Å Mn···Mn separations are present, and the $S = 2$ $\mathrm{Mn^{III}}$ sites are not bonded to a radical. Thus, $[\mathrm{Mn^{III}TPP}][\mathrm{TCQMI}]$ is best formulated as $\{[\mathrm{Mn^{III}TPP}]^+\}_2[\mathrm{TCQMI}]_2^{2-}$. The Mn−NCN−Mn linkages lead to one-dimensional chains that are cross-linked by the σ-$[\mathrm{TCQMI}]_2^{2-}$ dimer. This leads to a honeycomb two-dimensionally layered structure with 24-membered rings (Figure 1b). This motif is similar to that reported for tetrakis(2,4,6-triphenylmethyl)porphinatomanganese(III) ($[\mathrm{TCNQ}]^{\bullet-}$; **1**), which possesses $[\mathrm{TCNQ}]_2^{2-}$;[9a] however, the porphyrin ring is planar. The porphyrin plane warping observed for $[\mathrm{Mn^{III}TPP}]_2[\mathrm{TCQMI}]_2$ is attributed to greater steric interactions for the shorter Mn−NCN−Mn (vs Mn−NCCCN−Mn).

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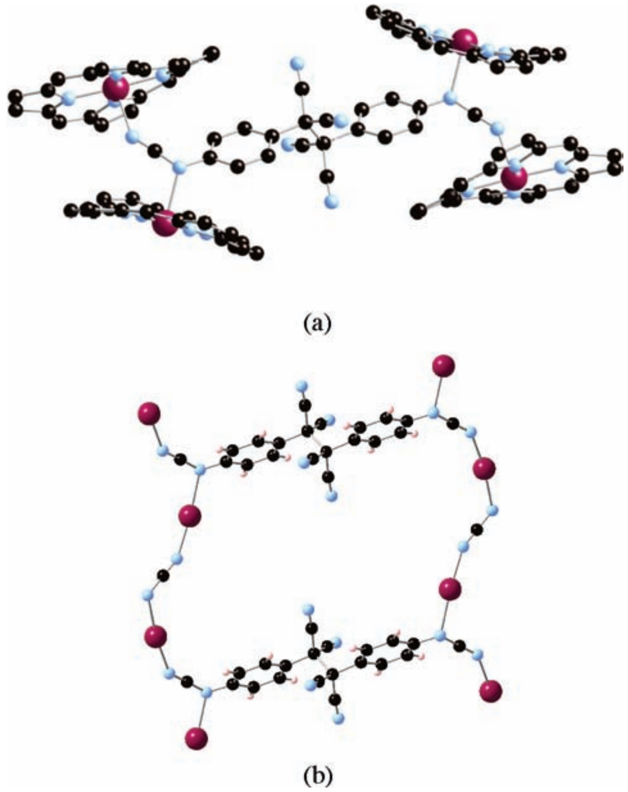

Figure 1. Structure of $[\mathrm{Mn^{III}TPP}]_2[\mathrm{TCQMI}]_2$ possessing $[\mathrm{TCQMI}]_2^{2-}$ (a) and the 24-membered ring connecting the chains (b). Color code: Mn, red; N, light blue; C, black.

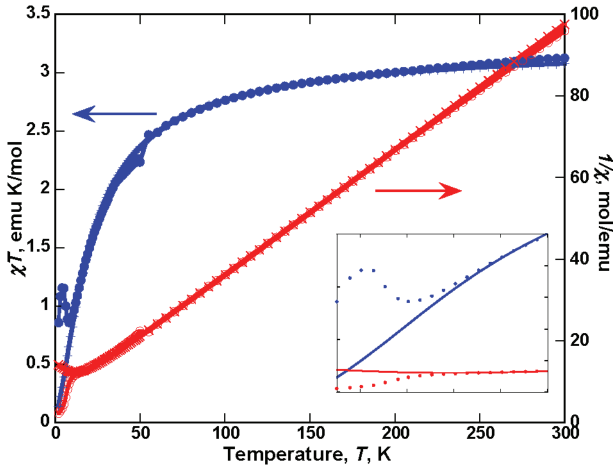

Figure 2. $\chi T(T)$ (●), $\chi^{-1}(T)$ (○), and fit (+) of $[\mathrm{Mn^{III}TPP}]_2$-$[\mathrm{TCQMI}]_2$ to eq 1.

$\chi T(T)$[18] of $[\mathrm{Mn^{III}TPP}]_2[\mathrm{TCQMI}]_2$ is 3.13 emu·K/mol at 300 K, in accordance with the spin-only expectation of 3.00 emu·K/mol for $S = 2$ $\mathrm{Mn^{III}}$ and diamagnetic $[\mathrm{TCQMI}]_2^{2-}$. This is comparable to that reported for **1**.[9a] Unlike **1**, however, upon cooling, $\chi T(T)$ decreases, and fitting $\chi T(T)$ above 20 K to the Curie−Weiss expression, $\chi \propto (T - \theta)^{-1}$, gives $\theta = -19.2$ K, indicative of significant antiferromagnetic coupling (Figure 2). This deviates from the $[\mathrm{Mn^{III}TPP}]_2[\mathrm{TCNE}]_2$ family of ferrimagnets because they have effective θ values that are significantly positive. Above 15 K, the $\chi T(T)$ data were fit to a one-dimensional chain model, eq 1, developed by Fisher and later modified by Smith and Friedberg,[19] with $g = 2.08$ and $J/k_B = -2.00$ K (-1.39 cm^{-1} and -4.00 cal/mol).

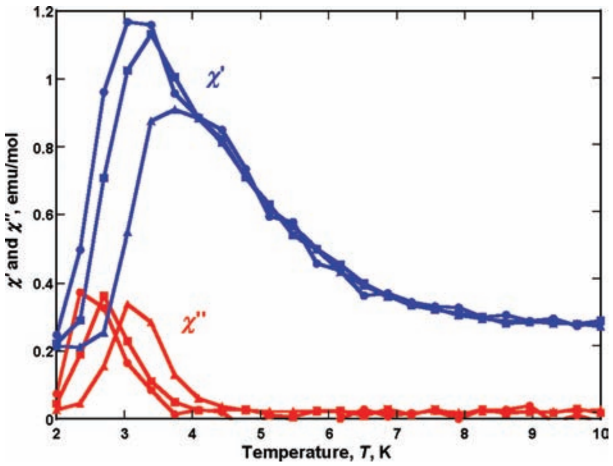

Figure 3. In-phase, $\chi'(T)$, and out-of-phase, $\chi''(T)$, susceptibility at 33 (●), 100 (■), and 1000 (▲) Hz.

$\chi T(T)$ continues to decrease with a decrease in the temperature until ~8 K, where it begins to rise to a maximum of 1.19 emu·K/mol at 4 K before decreasing again. The low magnetization is thought to arise from the spin canting of the $\mathrm{Mn^{III}}$ spin sites.

Evidence of magnetic ordering can be seen from the in-phase, $\chi'(T)$, and out-of-phase, $\chi''(T)$, components of the alternating-current (ac) susceptibility (Figure 3). The peak of the 33 Hz component occurs at 3.65 K, while the rise in $\chi''(T)$ upon cooling at 3.76 K provides another value of T_c, which averages 3.7 K.

$$\chi T = \frac{Ng^2\mu_B^{\,2}S(S+1)(1-u)}{3k_BT(1+u)}$$
$$u = \frac{T}{T_0} - \coth\frac{T_0}{T} \quad \text{and} \quad T_0 = \frac{2JS(S+1)}{3k_BT} \qquad (1)$$

Both $\chi'(T)$ and $\chi''(T)$ are frequency-dependent below 4 K, indicating either a spin glass or superparamagnetic state.[20]

This ordering temperature is in close agreement with the bifurcation temperature (T_b) observed below ~3.2 K observed from the zero-field- and field-cooled magnetization data (not illustrated). The origin of the canted antiferromagnetic/weak ferromagnetic ordering is attributed to the close proximity of the $\mathrm{Mn^{III}}$ sites. Similar behavior is seen in $\mathrm{Mn^{III}}$Salen sites bridged by HNCN in a $\mu_{1,3}$ mode with ordering temperatures observed below 2.5 K.[15] However, in contrast to these HNCN-bridged $\mathrm{Mn^{III}}$ compounds, no hysteresis loop is evident for $[\mathrm{Mn^{III}TPP}]_2[\mathrm{TCQMI}]_2$ and saturation magnetization is not achieved at 9 T.

Thus, the three-atom conjugated bridging NCN provides a pathway to stabilize magnetic ordering, as a canted antiferromagnet (weak ferromagnetic), which has not been observed for the conjugated five-atom NCCCN bridging group.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic data in CIF format for $[\mathrm{Mn^{III}TPP}]_2[\mathrm{TCQMI}]_2$ (CCDC 805691). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) TCQMI was synthesized by the modifying syntheses of Hyatt [Hyatt, J. A. *J. Org. Chem.* **1983**, *48*, 129] and Itoh and co-workers [Iwatsuki, S.; Itoh, T. T.; Itoh, H. *Chem. Lett.* **1988**, *17*, 1187]. Mn(TPP)(py) was formed following the scheme outlined by Basolo [Jones, R. D.; Summerville, D. A.; Basolo, F. *J. Am. Chem. Soc.* **1978**, *100*, 4416]. Reactions involving the formation of the TCQMI radical were carried out in an inert-atmosphere glovebox. $[\mathrm{Mn^{III}TPP}]_2[\mathrm{TCQMI}]_2$ was formed by dissolving TCQMI (12.8 mg, 0.071 mmol) and $\mathrm{Mn^{II}}$-(TPP)(py) (62.0 mg, 0.0731 mmol) in 20 mL of CH_2Cl_2 each, with the porphyrin solution being dark green/black. The solutions were then filtered and combined, but no color change could be discerned because of the dark coloring of the manganese solution. After the solution had stirred for 4 h at room temperature, the mixture was layered with an equal volume of hexanes (40 mL) and left to stand for 3 days in an inert-gas glovebox. This solution was filtered, capturing dark green/black crystals, which were washed with two 5 mL portions of CH_2Cl_2. Yield = 11.4%. IR (KBr; $\mathrm{cm^{-1}}$): 2188 w, 2140 sh, 2106 br.

(8) [MnTPP][TCQMI]: $C_{54}H_{32}MnN_8$, monoclinic, space group $P2_1/c$, a = 17.6731(15) Å, b = 22.610(2) Å, c = 11.5115(9) Å, β = 107.230(6)°, V = 4393.5(6) $\mathrm{Å^3}$, Z = 4, T = 100(2) K, ρ_{calc} = 1.282 $\mathrm{g/cm^3}$, R1 = 0.0578, wR2 = 0.1430.

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