Structure and magnetostructural correlation of ferrimagnetic meso-tetraphenylporphinatoman-ganese(III) dimethyl-*N,N'*-dicyanoquinone diiminide, $[\text{MnTPP}]^+[\text{Me}_2\text{DCNQI}]^-$

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Abstract: The structure $[\text{Mn}^{\text{III}}\text{TPP}][\text{Me}_2\text{DCNQI}]$ (TPP = tetraphenylporphinato; Me_2DCNQI = 2,5-dimethyl-*N,N'*-dicyanoquinone-diimine) has been determined from X-ray powder diffraction data. The nonsolvated structure is composed of linear (1-D) chains of alternating $[\text{Mn}^{\text{III}}\text{TPP}]^+$ and $\mu\text{-}[\text{Me}_2\text{DCNQI}]^-$ with intrachain $\text{Mn}\cdots\text{Mn}$ separations of 12.83 Å, and a $\text{Mn}\text{--}\text{N}_{\text{DCNQI}}$ distance of 2.18 Å. The dihedral angle between the mean $\text{Mn}(\text{N}_4)_{\text{TPP}}$ and $[\text{Me}_2\text{DCNQI}]^-$ planes, and the $\text{Mn}\text{--}(\text{N}\text{--}\text{C})_{\text{DCNQI}}$ angle are 84.18° and 143.6°, respectively. $[\text{Mn}^{\text{III}}\text{TPP}][\text{Me}_2\text{DCNQI}]$ has a T_c of 4.3 K from the 10 Hz $\chi''(T)$ data, 2-K coercivity of 5,600 Oe, and 6,300 emuOe/mol remnant magnetization that are reduced from that observed for related materials, and their inclusion extends the magnetostructural correlation between the intrachain coupling and both the dihedral angle between the mean $\text{Mn}(\text{N}_4)_{\text{TPP}}$ and $[\text{TCNE}]^-$ (TCNE = tetracyanoethylene) planes and $\text{Mn}\text{--}(\text{N}\text{--}\text{C})_{\text{TCNE}}$ angles. This is in accord with the intrachain coupling arising from the overlap of the Mn^{III} d_{z^2} -like singly occupied molecular orbital (SOMO) and the z component of the $[\text{TCNE}]^- \pi^*$ (π_z^*) SOMO, which increases with decreasing dihedral angle between the mean $\text{Mn}(\text{N}_4)_{\text{TPP}}$ and $[\text{TCNE}]^-$ planes and $\text{Mn}\text{--}(\text{N}\text{--}\text{C})_{\text{TCNE}}$ angle.

Keywords: metalloporphyrin, magnetic ordering, ferrimagnet, crystal structure

Illustration of the overlap leading to spin coupling arising from the Mn^{III} d_{z^2} -like and $\pi^*\text{-}[\text{TCNE}]^-$ SOMOs.

High-resolution synchrotron powder diffraction data and Rietveld fits to the data for [MnTPP][Me₂DCNQI]. The lower trace is the difference (measured-calculated) plotted to the same vertical scale.

Segment of the chain structure for [MnTPP][Me₂DCNQI] (the phenyl rings are omitted for clarity).

View along the chain (*b*) axis for [MnTPP][Me₂DCNQI] showing the interchain interactions.

Interchain interactions [and important distances (Å)] between unique out-of-registry chains of I–II (a), I–III (b), and II–IV (d), and in-registry I–IV (c).

$\chi(T)$ for [MnTPP][Me₂DCNQI] at 1000 Oe applied field.

$\chi^{-1}(T)$ (+) and $\chi T(T)$ (x) and fit of the latter to the Seiden expression solid line [MnTPP][Me₂DCNQI].

Hysteresis of [MnTPP][Me₂DCNQI] at 2 K.

$\chi'(T)$ (●) and $\chi''(T)$ (▲) for [MnTPP][Me₂DCNQI] at 10 (●, ▲), 100 (●, ▲), and 1000 (●, ▲) Hz.

Inverse correlation between the dihedral angle and the θ' (red), and the direct correlation between the dihedral angle and J_{intra} coupling obtained from the Seiden fit (blue) for a series of [MnPor]⁺ cations with [TCNE][−] (●), and DCNQI-based (▲) radicals.