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Structure and Magnetic Properties of (*meso*-Tetraphenylporphinato)manganese(III) Pentacyanopropenide, $[\mathrm{Mn^{III}TPP}]^+[\mathrm{C_3(CN)_5}]^-$. An Unusual Asymmetric Bridge-Bonding Mode for μ-$[\mathrm{C_3(CN)_5}]^-$

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To understand the detailed magnetic properties of the $[\mathrm{MnTPP}]^+[\mathrm{TCNE}]^{\bullet-}$[1] (TPP = *meso*-tetraphenylporphinato) family of molecule-based magnets, it is necessary to study related six-coordinate $[\mathrm{Mn^{III}TPP}]^+$ bound in the axial positions by diamagnetic nitrile groups in order to model the Mn(III) site. We sought to take advantage of the potential of diamagnetic $[\mathrm{C_3(CN)_5}]^-$ to bridge between two metal sites,[2c] although it frequently serves as an unbound counterion.[2a,b] Hence, $[\mathrm{Mn^{III}TPP}]^+[\mathrm{C_3(CN)_5}]^{\bullet-}$[3,4] was prepared.

Crystals of $[\mathrm{MnTPP}]^+[\mathrm{C_3(CN)_5}]^-\cdot x\mathrm{CH_2Cl_2}$ were grown from dichloromethane.[5] $[\mathrm{MnTPP}]^+[\mathrm{C_3(CN)_5}]^-$, Figure 1, forms parallel 1-D $\cdots\mathrm{D^+A^-D^+A^-}\cdots$ chains akin to that reported for $[\mathrm{MnTPP}]^+$-$[\mathrm{TCNE}]^-$, Figure 2.[1a,c] However, the cations do not lie parallel to one another but cant back and forth by ~20° (Figure 2) with respect to the chain axis. In contrast to previously reported structures of the cation, $[\mathrm{MnTPP}]^+$ is significantly puckered into a saddle shape as if the porphyrin ring were sterically encumbered.[1,6] The Mn−N$_{\mathrm{por}}$ bond distance average of 1.977(10) Å is comparable to the 2.000(3) Å observed for $[\mathrm{MnTPP}]^+[\mathrm{TCNE}]^-$.[1a,c] The axial Mn−N bond distance is 2.345 Å, which is comparable to that observed for [MnTPP][TCNE] (2.327 Å).[1a,c]

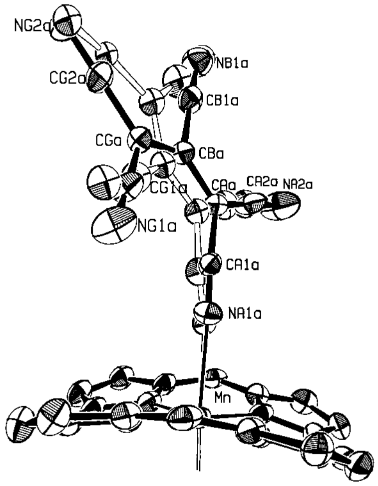

Figure 1. ORTEP[9] atom-labeling diagram showing the major (88%) (solid bonds) and minor (12%) (open bonds) orientation of the $[\mathrm{C_3(CN)_5}]^-$. The phenyl groups have been omitted for clarity, and the thermal ellipsoids are at the 50% probability level.

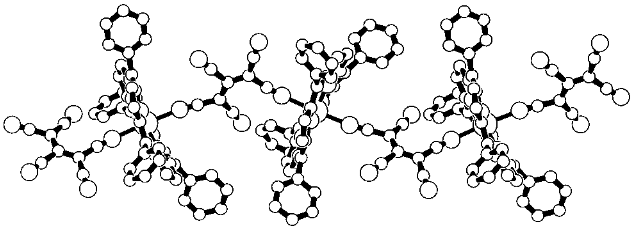

Figure 2. Linear chain of the title complex illustrating the asymmetric μ-bonding of the anion as well as the unusual saddle shape of the $[\mathrm{MnTPP}]^+$ cation.

The $[\mathrm{C_3(CN)_5}]^-$ ligand is disordered over two orientations in a 88:12 ratio. These orientations are related by a rotation about the Mn···Mn chain. This disorder has also been observed for unbound $[\mathrm{C_3(CN)_5}]^-$.[2b] The anion is not planar and has a 6.4° dihedral angle about CBla−CBa−CAa−CAla and an 8.3° dihedral angle about CBla−CBa−CGa−CG2a for the major orientation. The mean C≡N, C−CN, and C−CC bond distances are 1.134, 1.387, and 1.439 Å, as expected for a delocalized system. The C≡N distance is not altered upon bonding to the

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(3) A solution of $[\mathrm{Mn^{III}TPP}]\mathrm{Cl}$ (200 mg, 28.4 mmol) dissolved in 25 mL of dichloromethane was added dropwise to a slurry of equimolar $\mathrm{Ag[C_3(CN)_5]}$[4] in 25 mL of dichloromethane and stirred for 3 days. The reaction mixture was then filtered through diatomaceous earth to remove all traces of AgCl. The solution was layered with ~25 mL of mixed hexanes and left to sit undisturbed for ~2 weeks. The black crystals which formed were stored in this solution to prevent solvent loss. IR, υ_{CN} (Nujol): 2201(m), 1494(s) cm^{-1}.

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(5) Crystal data for $\mathrm{C_{54}H_{32}Cl_4MnN_9}$: $M_r = 1003.6$, orthorhombic *Pbca*, $a = 21.384(6)$ Å, $b = 17.425(10)$ Å, $c = 26.048(10)$ Å, $V = 9706(7)$ Å^3, $Z = 8$, $D_c = 1.257$ Mg/m^3, $\lambda = 0.710\,73$ Å, crystal size 0.44 × 0.25 × 0.16 mm, $T = -80$ °C, $2\Theta_{\max} = 24°$, $R_1 = 0.0743$, for 7612 independent reflections with $I > 4\sigma(I)$. The structure was solved by the MOLEN (*An Interactive Structure Solution Procedure*; Enraf-Nonius: Delft, The Netherlands, 1990) software and the structure refined by full-matrix least-squares procedures using SHELXL97 (Sheldrick, G. M. *SHELXL-97: A Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997). The disorder in the dichloromethane solvent and in the $[\mathrm{C_3(CN)_5}]^-$ anion was discovered and modeled using the program CHAIN [Sack, J. S. *J. Mol. Graph.* **1988**, *6*, 224] on a graphics workstation. The minor component of the anion was restrained to have a geometry similar to that of the major form, and the dichloromethane solvents were restrained to their standard geometry.

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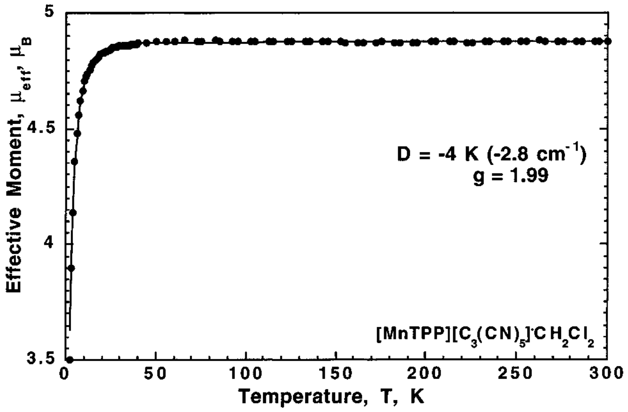

Figure 3. Temperature dependence of the moment, μ_{eff}, of $[\mathrm{Mn^{III}TPP}]^+[\mathrm{C_3(CN)_5}]^-$ and the fit of the data to eq 1 with $D = -4$ K and $g = 1.99$.

Mn(III). The major and minor orientations lie at 69.4 and 72° angles to the $\mathrm{MnN_4}$ plane with the two disordered components related by a 173° rotation about the Mn···Mn axis. $[\mathrm{Mn^{III}TPP}]^+[\mathrm{C_3(CN)_5}]^-$ forms 1-D chains composed of alternating cations and anions with the $[\mathrm{C_3(CN)_5}]^-$ anion asymmetrically μ-bridging between cations. The anion N1 and N5 atoms bond to the Mn with C−N−Mn angles of 163.2 and 173.1°, averaging 168°, Figure 2.

The magnetic moment, μ_{eff}, of $[\mathrm{Mn^{III}TPP}]^+[\mathrm{C_3(CN)_5}]^-\cdot x\mathrm{CH_2Cl_2}$ ($x = 1$) is presented as a function of temperature between 2 and 300 K in Figure 3. The susceptibility can be fit by the Curie−Weiss expression, $\chi \propto (T - \Theta)^{-1}$, with a Θ of -0.5 ± 0.5 K. The observed room-temperature effective moment, μ_{eff} $[\equiv(8\chi T)^{1/2}]$, is 4.88 μ_{B}, which is slightly reduced from the value of 4.90 μ_{B}, expected for an independent $g = 2$, $S = 2$ system,[6] and reflects a slightly reduced g value of 1.99 or that x is slightly above one. The $\mu_{\mathrm{eff}}(T)$ data can be fit to the $S = 2$ zero-field-splitting expression (using the Hamiltonian $H = DS_z^2 + g\mu_{\mathrm{B}}\mathbf{H}\cdot\mathbf{S}$)

$$\mu^2 = \frac{2g^2(\mathrm{e}^{-D/T} + 4\mathrm{e}^{-4D/T})}{1 + 2\mathrm{e}^{-D/T} + 2\mathrm{e}^{-4D/T}} + \frac{2g^2T(18 - 14\mathrm{e}^{-D/T} - 4\mathrm{e}^{-4D/T})}{3D(1 + 2\mathrm{e}^{-D/T} + 2\mathrm{e}^{-4D/T})} \tag{1}$$

where D, the zero-field-splitting parameter,[7] is −4.0 K (−2.8 cm^{-1}), Figure 3. This value falls within the range of −2.6 to −4.3 K reported for five-coordinate MnTTP(Cl)[7,8a,b,c] and MnTTP($\mathrm{ClO_4}$)[8b,d] as well as six-coordinate MnTPPCl(py)[7,8b,c] and MnTPP(1-methylimidazole)$_2$[8d] and is also comparable to values obtained for hydrated MnOEP(X) (X = Cl, Br, OAc, $\mathrm{ClO_4}$) complexes.[8d] The lack of magnetic coupling and ordering for $[\mathrm{Mn^{III}TPP}]^+[\mathrm{C_3(CN)_5}]^{\bullet-}$ but presence of strong coupling and ordering for the $[\mathrm{Mn(porphyrin)}]^+[\mathrm{TCNE}]^-$ family emphasizes the necessity to have the Mn(porphyrinate) bridged by spin-bearing ligands.

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Supporting Information Available: Tables of crystallographic details, positional and thermal parameters, interatomic distances, and intramolecular angles for $[\mathrm{Mn^{III}TPP}]^+[\mathrm{C_3(CN)_5}]^-\cdot x\mathrm{CH_2Cl_2}$ and a cation and anion labeling diagram for $[\mathrm{Mn^{III}TPP}]^+[\mathrm{C_3(CN)_5}]^-\cdot\mathrm{CH_2Cl_2}$ (11 pages). Ordering information is given on any current masthead page.

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