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Manganese(II) octabutoxynaphthalocyanine and its ferrimagnetic electron-transfer salt with TCNE

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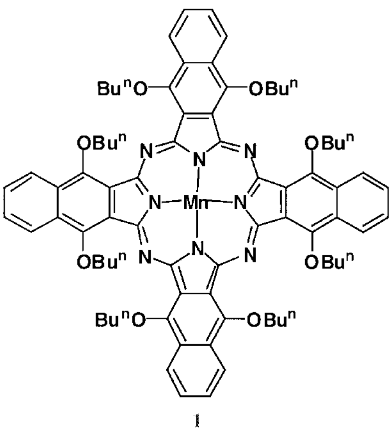
The magnetic susceptibility (χ) of 1,6,10,15,19,25,28,32-octa-*n*-butoxynaphthalocyaninatomanganese(III) tetracyanoethanide can be fit to a Curie–Weiss expression with $\theta = 54$ K for $T > 150$ K, and the $\chi T(T)$ data are consistent with linear chains and can be fit to a Seiden expression for alternating $S = 2$ and $S = 1/2$ antiferromagnetically coupled spin sites with a coupling constant, $J_{\rm intra}/k_{\rm B}$ ($H = -2JS_{\rm a}\cdot S_{\rm b}$) of -145 K. Hysteresis with a coercive field of 1.6 kOe was observed at 2 K. The magnetic ordering temperature, $T_{\rm c}$, determined from both the maximum in the 10 Hz ac susceptibility, $\chi'(T)$, and the irreversibility of low field zero field cooled/field cooled magnetization data, was determined to be 9.0 K. This is the first example of a metallophthalocyanine electron transfer salt that magnetically orders.

The preparation and characterization of molecule-based magnets is a growing area of contemporary interdisciplinary research.[1,2] Several families of TCNE-based (TCNE = tetracyanoethylene) materials exhibit magnetic ordering. The first organic magnet characterized was the electron transfer salt $[\mathrm{FeCp_2*}]^{\cdot+}[\mathrm{TCNE}]^{\cdot-}$ (Cp* = pentamethylcyclopentadienide) with an ordering temperature, $T_{\rm c}$, of 4.8 K.[3] This work led to the discovery of the first room-temperature organic magnet, the amorphous $\mathrm{V(TCNE)}_x\cdot y$(solvent) with $T_{\rm c} \approx 400$ K.[4] More recently, magnets based on metallomacrocycles and $[\mathrm{TCNE}]^{\cdot-}$ exemplified by [MnTPP][TCNE]·2PhMe ($\mathrm{H_2TPP}$ = *meso*-tetraphenylporphyrin) ($T_{\rm c} = 14$ K)[5] have been the focus of intensive research.[6]

Primarily due to their low solubility, phthalocyanine-based magnets have not been extensively studied, with the majority of work in this area limited to highly doped poorly characterized metallophthalocyanines.[7] An exception is [MnPc][TCNE] ($\mathrm{H_2Pc}$ = phthalocyanine), which exhibits ferromagnetic coupling, but not magnetic ordering.[8] Recent advances in soluble phthalocyanines have enabled their use in many aspects of solid state chemistry including metal-like conductors,[9] liquid crystals[10] and Langmuir–Blodgett (LB) films.[11] Recently, we have focused on substituted phthalocyanines as a means of increasing the solubility of phthalocyanines and subsequently isolating the resulting electron-transfer salts with TCNE with 1-D structures. Herein, we describe the synthesis and characterization of 1,6,10,15,19,25,28,32-octa-*n*-butoxynaphthalocyaninatomanganese(II), $\mathrm{Mn^{II}Nc(OBu)_8}$ **1**, and $\mathbf{1}^{+}[\mathrm{TCNE}]^{\cdot-}$; the first example of a phthalocyanine electron transfer salt exhibiting magnetic ordering.



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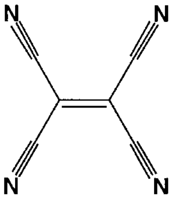

TCNE

Formation of **1**[OAc] was achieved by direct metal insertion into dilithiumphthalocyanine,[12] $\mathrm{Li_2Nc(OBu^n)_8}$, or by metallation of $\mathrm{H_2Nc(OBu^n)_8}$ with $\mathrm{Mn(OAc)_2\cdot 4H_2O}$ in DMF.[13] Reactions of **1**[OAc] with the strong acid $\mathrm{H_2TCNE}$ (p$K_{\rm a} = 3.6$) in the presence of TCNE[14,15] to form acetic acid and **1**[TCNE] were unsuccessful as impurities contaminated the product.

1 was prepared by the reduction of **1**[OAc] with sodium borohydride in a methanol/pyridine mixture using standard Schlenck techniques.[16] The solvent was removed and the product extracted from the crude reaction mixture and subsequently recrystallized from a mixture of dichloromethane and hexanes. UV/visible absorption spectroscopy of these products confirmed the presence of both the desired $\mathrm{Mn^{II}}$ product and its μ-oxo $\mathrm{Mn^{III}}$ dimer as an impurity.[17]

Additionally, a second method was utilized that is a modification from a recently published synthesis by Ricciardi *et al.*[18] by metallation of free-base phthalocyanine in propanol with $\mathrm{Mn^{II}(OAc)_2\cdot 4H_2O}$ under an inert atmosphere. The corresponding dipyridine complex of **1** can be isolated from the reaction mixture without further purification. Purity was confirmed by UV/Vis spectroscopy, which showed no evidence of $[\mathrm{Mn^{III}Nc(OBu^n)_8}]^{+}$ or $\mathrm{H_2Nc(OBu^n)_8}$ in the spectrum.

$\mathrm{Mn^{II}Nc(OBu)_8}$ **1** is an electron-rich $\mathrm{Mn^{II}}$ complex prone to oxidation in non-coordinating solvents such as toluene, chlorobenzene and dichloromethane.[19] In coordinating solvents such as acetonitrile, tetrahydrofuran and pyridine, the blue-green color of the $\mathrm{Mn^{II}}$ persists only for minutes in the absence of oxygen. Unlike unsubstituted $\mathrm{Mn^{II}Nc}$, **1** reacts with trace oxygen in highly coordinating solvents to from the μ-oxo dimer as evidenced by the 938 nm peak in the UV/vis spectrum.[20] This enhanced reactivity is attributed to electron-donation from the alkoxy substituents into the phthalocyanine macrocycle making the $\mathrm{Mn^{II}}$ electron-rich and prone to oxidation.

The Q-band absorption of phthalocyanines arises from the π–π^* transition of the phthalocyanine macrocycle and is particularly sensitive to slight changes in its electronic structure,[19] and occurs at 938 nm for $\mathbf{1}^{+}$ which is significantly red-shifted when compared to unsubstituted $[\mathrm{Mn^{III}Pc}]^{+}$ (718 nm).[21] The Q-band absorption of **1** in pyridine is observed at 941 nm, similarly red shifted with respect to unsubstituted $Mn^{II}Pc$ (667 nm) in pyridine.

1 shows one metal-based [Mn(III) to Mn(II)] reduction wave at −0.33 V, and two ring-based oxidation waves centered at 0.29 and 0.60 V (*vs.* SCE) respectively, Fig. 1. Similar ring-based oxidation values were observed for 2,3-$(C_8H_{17}O)_8PcFe^{II}[Bu^tNC]_2$ (0.38 V) and 1,4-$(C_8H_{17}O)_8PcFe^{II}[Bu^tNC]_2$ (0.22 V).[9]

Reaction of **1** with TCNE leads to black $[Mn^{III}Nc\text{-}1,6(OBu)_8]^+[TCNE]^{\bullet-}$, $\mathbf{1}^+[TCNE]^{\bullet-}$.[22] The infrared spectrum of **1**[TCNE] is consistent with the presence of $[TCNE]^{\bullet-}$ as indicated by the shift in the *ν*(CN) from 2259m and 2221s cm^{-1} for neutral TCNE to 2188m and 2130s cm^{-1} consistent with σ-*trans*-μ-*N*-bound $[TCNE]^{\bullet-}$ as observed for 1-D chain structures of this type.[23] Variable temperature IR studies of **1**[TCNE] do not show spectral changes suggesting no phase transition between 20 and 180 °C. Thermogravimetric analysis, TGA, coupled with quadrupole mass spectroscopy of **1**[TCNE] over the range 40 to 500 °C shows no evidence of solvent loss.[24]

The temperature dependence (2 to 300 K) of the magnetic susceptibility, χ, for **1**[TCNE] can be fit to a Curie–Weiss expression, $\chi \propto 1/(T-\theta)$, with $\theta = 54$ K[25] ($150 < T < 300$ K), Fig. 2. This value is lower then that observed for α-[MnPc][TCNE] (73 K) or for [MnTPP][TCNE] (61 K).[5] The observed room temperature effective moment, $\mu_{eff} = (\chi T)^{1/2}$, of **1**[TCNE], is 5.27 μ_B, near the expected value of 5.20 μ_B for isotropic independent $g = 2$, $S = 2$, and $S = 1/2$ radicals. At lower temperatures the moment $\mathbf{1}^+[TCNE]^{\bullet-}$ increases due to the correlation of uncompensated moments, reaching a maximum of 13.4 μ_B at 15.5 K.

The 1-D ferrimagnetic nature of **1**[TCNE] is also evident in the $\chi T(T)$ data, which can be modeled by the Seiden expression[26] for isolated chains of antiferromagnetically $S = 2$ and $S = 1/2$ spin sites with a J_{intra}/k_B of −145 K (−100 cm^{-1}, −201 cal) ($H = -2J_{intra}S_a \cdot S_b$), Fig. 2. The sign and magnitude of J_{intra} suggests strong intrachain antiferromagnetic coupling. The data fit remarkably well above 16 K; however, below 16 K the prediction exceeds the data suggesting antiferromagnetic interactions between chains begin to dominate.[27] Further, the goodness-of-fit of the Seiden expression suggests $\mathbf{1}^+[TCNE]^{\bullet-}$ consists of isolated chains with minimal interchain interactions. This is probably due to the large size of the substituted naphthalocyanine macrocycle effectively pushing chains apart while minimizing interdigitation as observed for [MnPc][TCNE].[8] As a consequence of ferrimagnetic coupling within the chain, $\chi T(T)$ is predicted to exhibit a minimum at ≈450 K, which cannot be verified.

Magnetic ordering was observed from the peaks in temperature dependences of the ac susceptibility and the zero field cooled/field cooled (ZFC/FC) magnetization data, as well as observation of hysteresis. A peak in the absorptive, $\chi'(T)$, component of the low frequency (10 Hz) ac susceptibility, frequently used to define the ordering temperature in this class of materials, was observed at 9.0 K, Fig. 3. Both $\chi'(T)$ and $\chi''(T)$ are frequency, ω, dependent indicative of spin-glass behavior, and/or disorder/frustration of the spin lattice. The amount of disorder can be parameterized by ϕ [$\phi = (\Delta T_f / T_f \Delta \log(\omega))$],[28] which for $\mathbf{1}^+[TCNE]^{\bullet-}$ is 0.19 indicating a highly disordered material.[27] The ordering temperature for a spin glass is commonly referred to as the freezing temperature, T_f, and may be determined independently by the divergence of the ZFC/FC studies at low fields. The position of this divergence in the ZFC/FC or bifurcation temperatures, T_b, for **1**[TCNE] at 0.1, 1.0 and 10.0 Oe was found to be 6.2, 7.1, and 9.0 K respectively, Fig. 4. The field dependence of bifurcation is consistent with a highly disordered spin glass material in good agreement with the large value of ϕ (0.19).[28] Although the origin of the observed magnetic disorder is not fully understood, it is probably a consequence of structural disorder.

The field dependence of the magnetization at 2 K, *M*(*H*), for $\mathbf{1}^+[TCNE]^{\bullet-}$ displays metamagnet-like behavior. At 2 K a slow rise in magnetization with increasing field, *H*, is observed until a critical field, H_c, of 24.0 kOe is reached which is followed by a rapid increase to 18 600 emu Oe mol^{-1} at 5 T. This value is substantially lower than the expectation for ferromagnetically coupling, *i.e.*, $S_{Tot} = 2 + 1/2 = 5/2$, of 27 925 emu Oe mol^{-1}, and higher than the expectation for

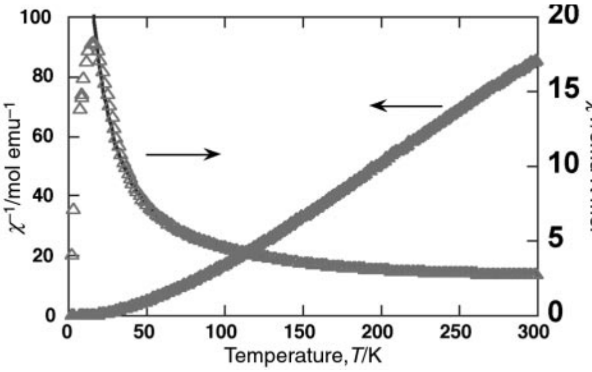

Fig. 2 Reciprocal molar magnetic susceptibility, χ^{-1} (△), and moment, μ_{eff} (▲), as a function of temperature for **1**[TCNE]. Line represents a fit to the predications for alternating quantum/classical spin ferrimagnetic chains (see text).

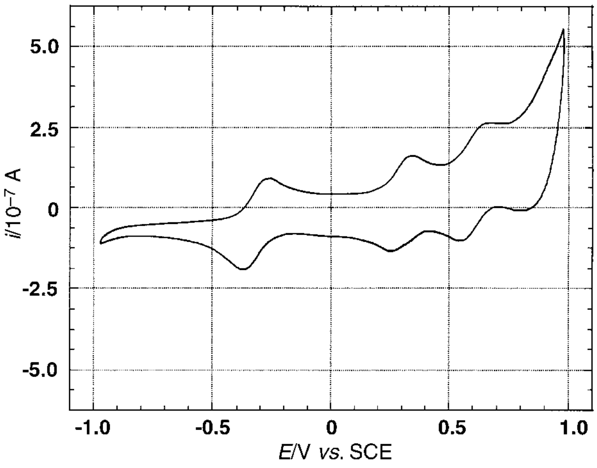

Fig. 1 Typical cyclic voltammogram of $MnNc(OBu^n)_8py$, **1**py, in a dichloromethane solution containing 0.1 M $[Bu^n_4N][PF_6]$ as a supporting electrolyte at a scan rate of 100 mV s^{-1}.

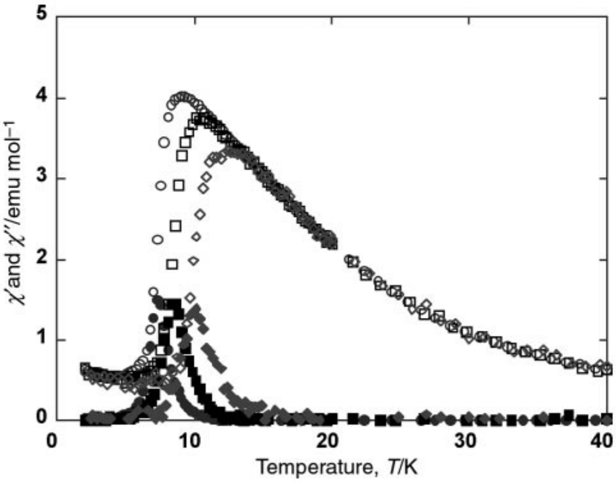

Fig. 3 Absorptive, χ', and dispersive, χ'', ac susceptibility as a function of temperature taken at 10 (○, ●), 100 (□, ■), and 1000 (◇, ◆) Hz at zero applied dc field (<0.5 Oe) and 1 Oe applied ac field for **1**[TCNE].

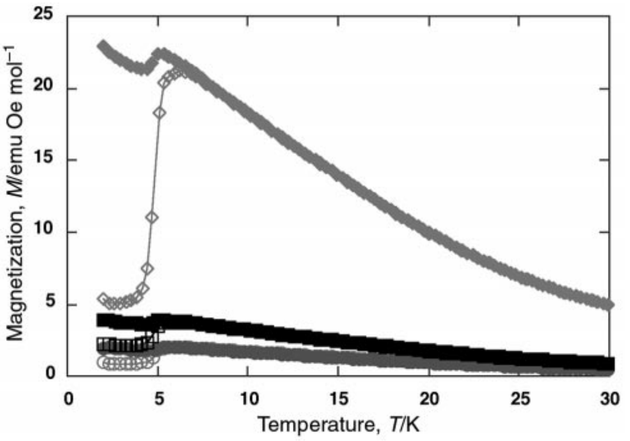

Fig. 4 Zero field cooled (open)/field cooled (closed) magnetization at 10 (○, ●), 1 (□, ■), and 0.1 (◇, ◆) Oe fields for **1**[TCNE].

antiferromagnetically coupled, *i.e.*, $S_{\mathrm{Tot}}=2-1/2=3/2$, of 16 755 emu Oe mol^{-1}. Similar behavior was observed for [MnTClPP][TCNE]·2CH$_2$Cl$_2$ (H$_2$TClPP = *meso*-tetrakis(4-chlorophenyl)porphyrin)[25] and α-[FeCp*$_2$][TCNQ][29] (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane) which also display metamagnetic behavior. Hysteresis was observed for $\mathbf{1}^{+}$[TCNE]$^{\bullet -}$ with a coercive field, H_{cr}, of 16.8 kOe at 2 K.

The $\mathbf{1}^{+}$[TCNE]$^{\bullet -}$ complex exhibits a θ value of 54 K indicative of strong magnetic coupling. Due to the large size of the naphthalocyanine, macrocycle interchain distances are expected to be large, thus each chain behaves more like idealized 1-D systems. Consequently, the magnetic data fit remarkable well to a Seiden model above 16 K. At low temperature, 3-D ordering was observed below 9 K. The origin of 3-D ordering and factors controlling 1-D chain formation are presently under investigation.

Acknowledgements

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12 Synthesis: All manipulations were carried out under an atmosphere of nitrogen using standard Schlenck techniques or in a Vacuum Atmospheres DriLab®. All solvents used were predried and distilled from appropriate drying agents. H$_2$Nc(OBu)$_8$ was obtained from BASF and used as received, and TCNE was resublimed prior to use. Physical Methods: The dc magnetic susceptibility was determined on a Quantum Design MPMS-5XL 5 T SQUID as previously reported.[26] In addition to correcting for the diamagnetic contribution from the sample holder, core diamagnetic corrections of -1062 and -60.0×10^{-6} emu mol^{-1} were used for MnNc(OBu)$_8$ and TCNE respectively. The thermal properties were studied on a TA Instruments Model 2050 thermal gravimetric analyzer equipped with an electron impact mass spectrometer (TGA) (ambient to 1000 °C) located in a Vacuum Atmospheres DriLab® under argon to study air and moisture sensitive samples. Samples were placed in an aluminium pan and heated at 20 °C min^{-1} under a continuous 10 mL min^{-1} nitrogen flow. Infrared spectra (600–4000 cm^{-1}) were obtained on a Bio-Rad FT-40 spectrophotometer. UV/visible spectra were obtained on a Hewlett Packard UV/Vis 590 or a Cary 17 spectrophotometer. Spectra were taken on small unweighed samples to ascertain the peak positions and relative intensities only. Electrochemical measurements were made using a conventional three-electrode cell equipped with a 2 mm platinum disk working electrode, a Pt wire counter electrode and a Ag/Ag$_2$O reference electrode. Solutions were composed of the analyte dissolved in CH$_2$Cl$_2$ containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as the electrolyte. The scan rate was 100 mV s^{-1}. Voltammetric curves were obtained using an EG&G Princeton Applied Research model 273 Potentiostat. All electrochemistry was performed at room temperature in a "dry" Vacuum Atmospheres Drilab®. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA.

13 [Mn$^{\mathrm{III}}$Nc(OBu)$_8$]$^{+}$[OAc]$^{-}$, **1**[OAc]: In a 1 L three-neck flask equipped with a magnetic stirrbar H$_2$Nc(OBu)$_8$ (10.01 g, 7.71 mmol), Mn(OAc)$_2$·4H$_2$O (4.02 g, 1.81 mmol), NaOAc (10.12 g, 124.4 mmol) and 150 mL of DMF were heated to reflux for 90 min under dry nitrogen. The resulting black solution was cooled to room temperature and a black microcrystalline precipitate was observed. The product was collected *via* vacuum filtration, and recrystallized from methanol–diethyl ether (1 : 1). Yield 7.62 g (61%) of **1**OAc. Anal. Calc. for C$_{82}$H$_{99}$MnN$_8$O$_{10}$ C, 69.77; H, 7.10; N, 7.94. Found: C, 69.51, H, 6.85; N, 7.03%. IR

(Nujol; ν/cm^{-1}), 1597s, 1515s and 1089s. UV/Visible (CH_2Cl_2, λ_{max}/nm) 938, 640 and 396.

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17 $Mn^{II}Nc(OBu)_8 \cdot HOC_3H_7$, **1**. *Method 1*: In a 100 mL Schlenk flask **1**OAc (530.1 mg, 0.41 mmol) was dissolved in 20 mL of a 1 : 1 mixture of methanol and pyridine. Sodium borohydride (105.0 mg, 1.81 mmol) was added in three portions over 30 min. The solution was heated to 60 °C for 40 min and allowed to cool to room temperature. The solvent was removed under reduced pressure resulting in a blue powder, which was extracted with 3 × 50 mL of dry CH_2Cl_2. The solution was filtered and the filtrate was reduced to a volume of 30 mL and hexanes ($\approx$30 mL) added. The product was collected by vacuum filtration on a glass frit, yield 520.1 mg, 94.5%. *Method 2*: A Schlenk flask was charged with $H_2Nc(OBu)_8$ (500.0 mg, 0.3871 mmol), $Mn(OAc)_2 \cdot 4H_2O$ (500 mg, 0.203 mmol), 3 mL of pyridine and 300 mL of propanol, which formed a dark violet solution. This was heated to reflux for 72 h until TLC analyses showed no evidence of residual $H_2Nc(OBu)_8$. The resulting dark purple solution was reduced to 100 mL and cooled to room temperature yielding a dark-green precipitate. The product was collected *via* vacuum filtration, yield 400.0 mg (73%). Anal. Calc. for $C_{83}H_{96}N_8MnO_9$: C, 70.97; H, 6.89; N, 7.98. Found: C, 70.90, H, 6.62; N, 7.85%. UV/Visible (pyridine, λ_{max}/nm) 350, 414, 476, 548, 712. IR (Nujol; ν/cm^{-1}) 1594s, 1292s, 1073s. $E_{1/2}$/eV (CH_2Cl_2,[$Bu^n{}_4N$]PF_6) −0.33, 0.29, and 0.60.

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22 $[MnNc(OBu)_8]^+[TCNE]^{\bullet-}$, **1**[TCNE]. Filtered solutions of $Mn^{II}Nc(OBu)_8py$ (230 mg, 0.16 mmol) in 14 mL of toluene and TCNE (25 mg, 0.1952 mmol) in 7 mL of toluene were mixed and stirred under nitrogen at room temperature for 1 h and the reaction mixture was cooled to −20 °C for 48 h. The resulting black microcrystalline precipitate was collected by vacuum filtration, yield 170 mg (72%) of **1**[TCNE] as a purple-black microcrystalline powder. Anal. Calc. for $C_{86}H_{88}MnN_{12}O_8$: C, 70.14; H, 6.02; N, 11.41. Found: C, 69.90, H, 6.02; N, 11.43%. IR (Nujol; ν/cm^{-1}): ν(CN) 2188m, 2130s. Crystals suitable for X-ray structure determination have yet to be prepared.

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