

# [Mn<sup>II</sup>(*t*-Bu)<sub>4</sub>salen]<sub>2</sub> and Its Reaction with TCNE

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IN DEDICATION TO THE LATE PROFESSOR OLIVIER KAHN FOR HIS PIONEERING CONTRIBUTIONS TO THE FIELD OF MOLECULAR MAGNETISM

**Mn<sup>II</sup>(*t*-Bu)<sub>4</sub>salen has been prepared and magnetically characterized as a dimer with weak intradimer coupling of  $J = -7.8 \text{ cm}^{-1}$  ( $J/k_B = 11 \text{ K}$ ) for  $H = -2J\mathbf{S}_a \cdot \mathbf{S}_b$ . The electron transfer salt of TCNE and Mn<sup>II</sup>(*t*-Bu)<sub>4</sub>salen exhibits weak anti-ferromagnetic coupling.** © 2001 Academic Press

## INTRODUCTION

Mn(II)porphyrins reduce TCNE (1) (TCNE = tetracyanoethylene) to form 1-D chains of [Mn<sup>III</sup>porphyrin]<sup>+</sup>[TCNE]<sup>-</sup> that magnetically order as ferrimagnets (2), with magnetic ordering temperatures as high as 28 K (3). In order to identify additional families of magnetically ordered materials, we targeted electron transfer salts of Mn<sup>II</sup>salen (salen = bis(salicylaldehyde)ethylenediamine). Mn<sup>II</sup>salen was originally synthesized as a catalyst to epoxidize olefin compounds (4). Electron transfer salts of Mn<sup>II</sup>salen were prepared with TCNQ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane) from methanol and yielded two 1-D chain-structured materials containing methanol, which did not exhibit significant intrachain magnetic coupling (5). Due to the low solubility of Mn<sup>II</sup>salen in most solvents, methanol was used as the solvent, which then coordinates to the metal centers. To increase the solubility in low-polarity solvents and thus eliminate the need for a coordinating solvent, we selected the [(*t*-Bu)<sub>4</sub>salen]<sup>2-</sup> ligand. Mn<sup>II</sup>(*t*-Bu)<sub>4</sub>salen (Scheme 1) was expected to be oxidized with TCNE in a noncoordinating solvent, producing 1-D chains. The polymerization should cause the high-spin, paramagnetic, highly conjugated systems to align and subsequently produce ferromagnetic properties as observed in the Mn(porphyrin) family of compounds (2, 3).

## EXPERIMENTAL

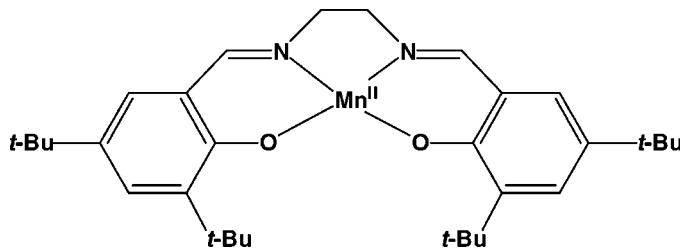
Proton sponge, MnBr<sub>2</sub>, and 3,5-di-*t*-butyl-2-hydroxybenzaldehyde were utilized as purchased from Aldrich.

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Ethylenediamine (en) was distilled over CaH<sub>2</sub> and TCNE was prepared by a literature procedure (6) and vacuum sublimed prior to use. Mn<sup>II</sup>salen was prepared by a literature method (7). NMR spectra were recorded on a Varian XL-300 spectrometer. IR spectra were recorded on a Bio-Rad FTS-40 FT-IR spectrometer as Nujol mulls or KBr pellets. Thermal properties were measured on a TA Instruments TGA 2050 thermogravimetric analyzer (TGA) coupled to a Thermolab quadrupole mass spectrometer. Magnetic measurements were made on a Quantum Design MPMS-5T SQUID magnetometer as described previously (8).

[Mn(NCMe)<sub>6</sub>](OTf)<sub>2</sub> (OTf = O<sub>3</sub>SCF<sub>3</sub>). A solution of 2.39 g (9.30 mmol) of AgOTf dissolved in 15 mL of MeCN was added to a stirred slurry of 1.00 g (4.66 mmol) MnBr<sub>2</sub> in 40 mL MeCN. After stirring for 1 h, the mixture was filtered to remove a gray solid. The colorless filtrate was reduced to 15 mL. Ether diffusion produced 1.78 g (64%) of pale-pink crystals. IR (Nujol): 2309, 2280 cm<sup>-1</sup>.

H<sub>2</sub>(*t*-Bu)<sub>4</sub>salen. Five grams (21.3 mmol) of 3,5-di-*t*-butyl-2-hydroxybenzaldehyde was added into the three-necked flask, provided with a condenser and two glass stoppers, and dissolved in 35 mL of absolute ethanol. The resulting mixture was heated to reflux. To the boiling mixture, 0.713 mL (10.7 mmol) of en was added dropwise, and the resulting bright yellow solution turned dark yellow, then precipitated a yellow solid. After complete en addition, the reaction was heated to reflux for an additional 10 min., then



SCHEME 1

cooled in an ice bath. The bright yellow crystals were filtered and washed with ethanol ( $3 \times 20$  mL). Yield (4.93 g; 90%). IR (Nujol): 1628, 1480, 1466, 1439, 1392, 1270, 1173, 1041, 973  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.26 (s, 5-*t*-Bu), 1.43 (s, 3-*t*-Bu), 3.93 (s, en ethylene protons), 7.1–7.4 (m, 4,6-H-Ar), 8.39 (s, Ar-CH-N) ppm.

$[\text{Mn}^{\text{II}}(t\text{-Bu})_4\text{salen}][\text{MeCN}]_{0.87}$ . The following synthesis was conducted under a nitrogen atmosphere, and in oxygen-free solvents. One gram (2.03 mmol) of  $\text{H}_2(t\text{-Bu})_4\text{salen}$  was added with 1.21 g of (2.03 mmol)  $[\text{Mn}(\text{NCMe})_6](\text{OTf})_2$  and 0.868 g of (4.05 mmol) of proton sponge into a Schlenk flask containing 40 mL of MeCN. The mixture was stirred for 1 h, during which time all solids dissolved, forming a homogeneous red-brown solution. The solution was evaporated to dryness, and the solids were extracted with 80 mL of toluene. This mixture was filtered to remove a white solid and the red-brown filtrate was evaporated to dryness. The red-brown solid was recrystallized in 500 mL boiling hexane to give orange needles (0.689 g; 41%). IR (Nujol): 1623, 1528, 1462, 1377, 1164, and 722  $\text{cm}^{-1}$ . TGA revealed that 6.18% mass was lost upon heating to 100°C. This corresponds to 0.87 acetonitrile per Mn.

$[\text{Mn}^{\text{III}}(t\text{-Bu})_4\text{salen}][\text{TCNE}][\text{toluene}]_{1.365}$ . The following synthesis was conducted under a nitrogen atmosphere.  $[\text{Mn}^{\text{II}}(t\text{-Bu})_4\text{salen}][\text{MeCN}]_{0.87}$  (0.125 g, 0.23 mmol) was dissolved into 5 mL of toluene, and TCNE (0.0293 g, 0.23 mmol) was dissolved into 10 mL of toluene. These two solutions were combined and produced a dark red-black solution. After stirring for 20 min., the solution was filtered to isolate a red-black powder. It was washed with toluene ( $5 \times 10$  mL) and dried under vacuum to produce 0.113 g

(73%) of product. IR (KBr or Nujol): 2146 (w), 2169 (s), 2182(s), 2199 (m)  $\text{cm}^{-1}$ . TGA analysis revealed the compound lost 18.71% mass at 130°C, which corresponds to 1.365 mol of toluene per Mn.

## RESULTS AND DISCUSSION

Initially,  $\text{Mn}^{\text{II}}\text{salen}$  was prepared and reacted with TCNE in toluene in an attempt to form the linear-chain compound. However, the  $\text{Mn}^{\text{II}}\text{salen}$  is only sparingly soluble in toluene, resulting in the contamination of products with the starting material. Therefore,  $\text{H}_2(t\text{-Bu})_4\text{salen}$  was prepared. Although many substituted derivatives of salen are known, there was no mention of the tetra-*tert*-butyl derivative. The  $\text{H}_2(t\text{-Bu})_4\text{salen}$  was prepared by a standard condensation reaction in ethanol in high yield (9); however, the metallation to form  $\text{Mn}^{\text{II}}(t\text{-Bu})_4\text{salen}$  proved to be difficult. Literature procedures effective for preparing  $\text{Mn}^{\text{II}}\text{salen}$  (7, 10) were ineffective due to the significantly increased oxygen sensitivity of  $\text{Mn}^{\text{II}}(t\text{-Bu})_4\text{salen}$  arising from the four electron-donating *t*-butyl groups. Hence, a new route based on aprotic solvents in a rigorously inert atmosphere was developed. The reaction of  $[\text{Mn}^{\text{II}}(\text{NCMe})_6](\text{OTf})_2$  with  $\text{H}_2(t\text{-Bu})_4\text{salen}$  formed  $\text{Mn}^{\text{II}}(t\text{-Bu})_4\text{salen}$  as orange needles. Attempts to grow crystals of suitable size for crystallography proved unsuccessful. The compound is freely soluble in many solvents including MeCN, dichloromethane, toluene, and diethyl ether.

The magnetic susceptibility,  $\chi$ , between 2 and 300 K of  $\text{Mn}^{\text{II}}(t\text{-Bu})_4\text{salen}$  was determined, Fig. 1. Above 150 K the data can be fitted to the Curie-Weiss expression,  $\chi \propto (T - \theta)^{-1}$ , with  $\theta = -34$  K as expected for an isolated

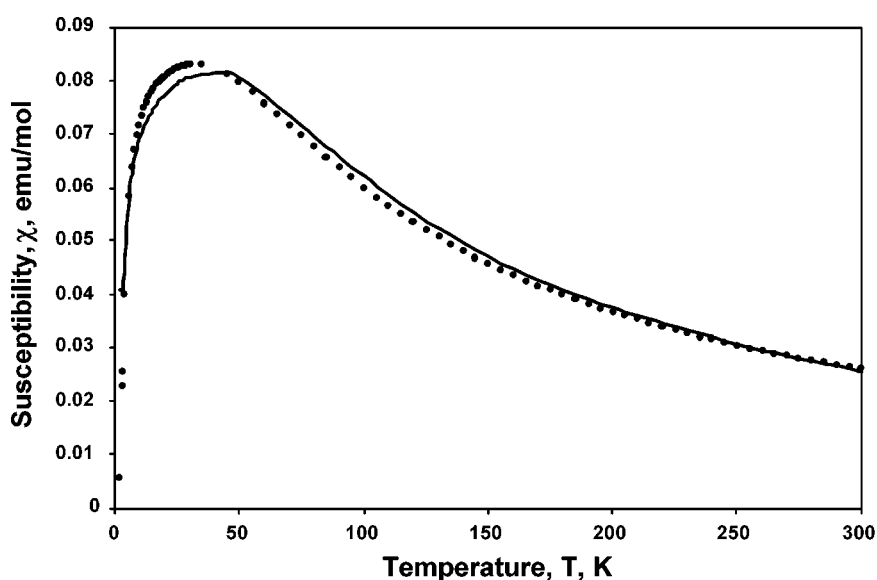


FIG. 1. Temperature dependence of the magnetic susceptibility,  $\chi$ , of  $\text{Mn}^{\text{II}}(t\text{-Bu})_4\text{salen}$ . The solid line is the best fit of Eq. [1].

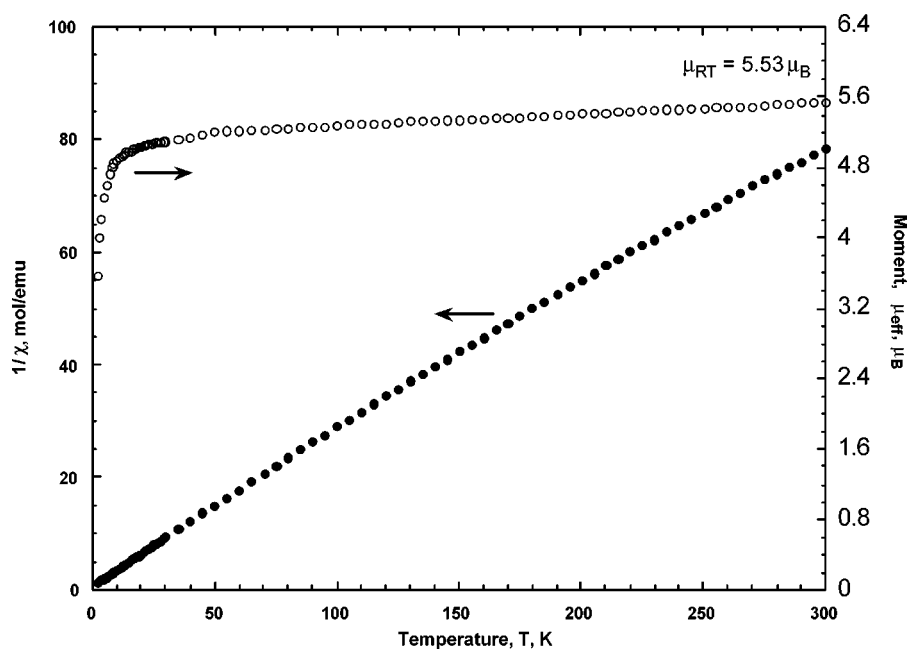


FIG. 2. Temperature dependence of the reciprocal magnetic susceptibility,  $1/\chi$ , and moment,  $\mu$ , of [Mn<sup>III</sup>(*t*-Bu)<sub>4</sub>salen][TCNE]. The solid line is the fit to the Curie–Weiss law.

Mn<sup>II</sup>  $S = \frac{5}{2}$  ion. The data, however, are best fitted to the Bleaney–Bowers-like expression for isolated  $S = \frac{5}{2}$  dimers,

$$\chi = \frac{2Ng^2\beta^2}{kT} \frac{e^x + 5e^{3x} + 14e^{6x} + 30e^{10x} + 55e^{15x}}{1 + 3e^x + 5e^{3x} + 7e^{6x} + 9e^{10x} + 11e^{15x}}, \quad [1]$$

assuming  $H = -2JS_a \cdot S_b$  (11) over the entire temperature range. The best fit produced a  $J = -7.8 \text{ cm}^{-1}$  ( $J/k_B = 11 \text{ K}$ ) (Fig. 1) in good agreement with the value of  $-6.5 \text{ cm}^{-1}$  ( $J/k_B = 9.4 \text{ K}$ ) reported for Mn<sup>II</sup>salen for data taken above 80 K (12). Hence, Mn<sup>II</sup>(*t*-Bu)<sub>4</sub>salen is a dimer, [Mn<sup>II</sup>(*t*-Bu)<sub>4</sub>salen]<sub>2</sub>, in the solid state. The stronger antiferromagnetic coupling for [Mn<sup>II</sup>(*t*-Bu)<sub>4</sub>salen]<sub>2</sub> with respect to [Mn<sup>II</sup>salen]<sub>2</sub> suggests that the former has a shorter intradimer separation arising from each moiety being more electron rich due to the electron-donating *t*-Bu groups. The experimentally determined room temperature moment of  $7.84 \mu_B$  is in agreement with the value of  $7.90 \mu_B$  obtained from Eq. [1]. Alternatively, the stronger coupling may be a consequence of differing direct or superexchange pathways, which must await a structural determination.

The redox reaction of the Mn<sup>II</sup>(*t*-Bu)<sub>4</sub>salen with TCNE proceeded quickly, forming a darkly colored product of [Mn<sup>III</sup>(*t*-Bu)<sub>4</sub>salen][TCNE][toluene]<sub>x</sub> ( $x = 1.365$ ) composition. The IR in the  $\nu_{\text{CN}}$  region exhibits four absorptions at 2199(m), 2182(s), 2169(s), and 2146(w)  $\text{cm}^{-1}$ . The magnetic susceptibility data were also measured between 2 and 300 K, which can be fitted to the Curie–Weiss law with

$\theta = -6.1 \text{ K}$ , Fig. 2. The small, negative  $\theta$  value indicates that the material exhibits weak antiferromagnetic coupling. This is in contrast to the [Mn<sup>III</sup>(porphyrin)[TCNE]<sub>x</sub>(solvent) family of materials that have positive  $\theta$  values (2). The low negative  $\theta$  indicates that the necessary chains are not formed and may be prohibited by the four *t*-Bu groups. As only two  $\nu_{\text{CN}}$  absorptions are expected from a uniform 1-D chain composed of  $\mu$ -[TCNE]<sup>•-</sup> (3, 8, 13), and four  $\nu_{\text{CN}}$  absorptions are observed, terminally bound [TCNE]<sup>•-</sup> or possibly multiple phases are present. In any event the observed antiferromagnetic coupling does not warrant further study for this compound.

## CONCLUSIONS

Mn<sup>II</sup>(*t*-Bu)<sub>4</sub>salen is extremely air sensitive and like Mn<sup>II</sup>salen is a dimer in the solid state. Reaction with TCNE leads to the formation of [Mn<sup>III</sup>(*t*-Bu)<sub>4</sub>salen][TCNE], which unlike the [Mn<sup>III</sup>porphyrin][TCNE] family of ferromagnets does not exhibit evidence of ferromagnetic coupling (i.e.,  $\theta < 0 \text{ K}$ ). [Mn<sup>III</sup>(*t*-Bu)<sub>4</sub>salen][TCNE] has four  $\nu_{\text{CN}}$  absorptions, suggesting the presence of either a terminally bound [TCNE]<sup>•-</sup> or the presence of more than one phase.

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