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# Magnetic Susceptibility and Ground-State Zero-Field Splitting in High-Spin Mononuclear Manganese(III) of Inverted N-Methylated Porphyrin Complexes: $\text{Mn}(\text{2-NCH}_3\text{NCTPP})\text{Br}$ #

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Magnetic Susceptibility and Ground-State Zero-Field Splitting in High-Spin Mononuclear Manganese(III) of Inverted N-Methylated Porphyrin Complexes:  $\text{Mn}(\text{2-NCH}_3\text{NCTPP})\text{Br}^\#$ Sheng-Wei Hung,<sup>†</sup> Fuh-An Yang,<sup>†</sup> Jyh-Horung Chen,<sup>\*,†</sup> Shin-Shin Wang,<sup>‡</sup> and Jo-Yu Tung<sup>\*,§</sup>

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The crystal structures of diamagnetic dichloro(2-aza-2-methyl-5,10,15,20-tetraphenyl-21-carbaporphyrinato-N,N',N'')-tin(IV) methanol solvate  $[\text{Sn}(\text{2-NCH}_3\text{NCTPP})\text{Cl}_2 \cdot 2(0.2\text{MeOH})]$ ; **6**  $\cdot 2(0.2\text{MeOH})$ ] and paramagnetic bromo(2-aza-2-methyl-5,10,15,20-tetraphenyl-21-carbaporphyrinato-N,N',N'')-manganese(III)  $[\text{Mn}(\text{2-NCH}_3\text{NCTPP})\text{Br}]$ ; **5** were determined. The coordination sphere around  $\text{Sn}^{4+}$  in **6**  $\cdot 2(0.2\text{MeOH})$  is described as six-coordinate octahedron (*OC-6*) in which the apical site is occupied by two transoid  $\text{Cl}^-$  ligands, whereas for the  $\text{Mn}^{3+}$  ion in **5**, it is a five-coordinate square pyramid (*SPY-5*) in which the unidentate  $\text{Br}^-$  ligand occupies the axial site. The *g* value of 9.19 (or 10.4) measured from the parallel polarization (or perpendicular polarization) of X-band EPR spectra at 4 K is consistent with a high spin mononuclear manganese(III) ( $S = 2$ ) in **5**. The magnitude of axial (*D*) and rhombic (*E*) zero-field splitting (ZFS) for the mononuclear Mn(III) in **5** were determined approximately as  $-2.4 \text{ cm}^{-1}$  and  $-0.0013 \text{ cm}^{-1}$ , respectively, by paramagnetic susceptibility measurements and conventional EPR spectroscopy. Owing to weak  $\text{C}(45)\text{---H}(45\text{A}) \cdots \text{Br}(1)$  hydrogen bonds, the mononuclear Mn(III) neutral molecules of **5** are arranged in a one-dimensional network. A weak Mn(III)  $\cdots$  Mn(III) ferromagnetic interaction ( $J = 0.56 \text{ cm}^{-1}$ ) operates via a  $[\text{Mn}(1)\text{---C}(2)\text{---C}(1)\text{---N}(4)\text{---C}(45)\text{---H}(45\text{A}) \cdots \text{Br}(1)\text{---Mn}(1)]$  superexchange pathway in complex **5**.

## Introduction

In general, Electron Paramagnetic Resonance (EPR) spectroscopy at conventional microwave frequencies [X-band,  $\sim 9 \text{ GHz}$  ( $0.3 \text{ cm}^{-1}$ ); Q-band,  $\sim 35 \text{ GHz}$  ( $1.2 \text{ cm}^{-1}$ )] is not applicable to “EPR-silent” systems with integral-spin ground states where the zero-field splitting (ZFS) is larger than the microwave quantum, in particular, where the ZFS interaction approaches axial symmetry.<sup>1–3</sup> Thus, conventional EPR studies of high-spin manganese(III) ( $d^4$ ,  $S = 2$ ) compounds are rather limited especially for the N-confused porphyrin (NCP) complex

(NCP is also known as inverted porphyrin or 2-aza-21-carbaporphyrin). Recently, essential progress has been observed in the literature concerning the synthesis and characterization of NCP and its derivatives. Hung et al.<sup>4</sup> reported the X-ray structure of a five-coordinate manganese(III) complex of N-confused 5,10,15,20-tetraphenylporphyrin  $\text{Mn}(\text{NCTPP})\text{Br}$  (**1**) (NCTPP, dianion of 5,10,15,20-tetraphenyl-N-confused porphyrin) and Harvey and Ziegler<sup>5</sup> described the structural characterization of a six-coordinate Mn(III) complex of  $\text{Mn}(\text{NCTPP})(\text{py})_2$  (**2**). Krzystek and co-workers<sup>6</sup> reported the high-frequency and -field electron paramagnetic resonance (HF-EPR) study of complex **2**. It turned out that the inversion of a single pyrrole ring of **2** greatly changes the equatorial ligand field exerted and leads to large magnitudes of both the axial and rhombic ZFS (respectively,  $D = -3.08 \text{ cm}^{-1}$ ,  $E = -0.61 \text{ cm}^{-1}$ ), which are unprecedented in other Mn(III) porphyrinoids.<sup>6</sup>

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<sup>†</sup> Dedicated to Prof. Rob Dunbar (Case Western Reserve University) on the occasion of his 65th birthday.

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Recently, Ziegler et al.<sup>7</sup> reported an improved methodology for the synthesis of 2-N-methyl-5,10,15,20-tetraphenyl-21-carbaporphyrin, 2-NCH<sub>3</sub>NCTPPH (**3**). Compound **3** in this work was prepared in the way described by the Ziegler group using CH<sub>3</sub>I and *p*-xylene in 48.6% yield. Unlike the NH tautomerism that exists in NCTPPH<sub>2</sub> (**4**),<sup>8</sup> the free base **3** has only one stable form. Thus, a placement of a Mn(III) ion ( $I = 5/2$ ) with a paramagnetism and a Sn(IV) ion ( $I = 1/2$ ) with a diamagnetism in a core of N-methylated carbaporphyrin provides a promising route to synthesize a paramagnetic complex, bromo(2-aza-2-methyl-5,10,15,20-tetraphenyl-21-carbaporphyrinato-N,N',N'')-manganese(I-II) [Mn(2-NCH<sub>3</sub>NCTPP)Br; **5**] and a diamagnetic complex, dichloro(2-aza-2-methyl-5,10,15,20-tetraphenyl-21-carbaporphyrinato-N,N',N'')-tin(IV) [Sn(2-NCH<sub>3</sub>NCTPP)Cl<sub>2</sub>; **6**]. This new diamagnetic compound **6** is used as a diamagnetic correction for **5** in the solid-state magnetic susceptibility measurements.<sup>9</sup> In this paper we focus on details of the manganese(III) electronic structure. Studies of temperature dependence of the magnetic susceptibility and of the effective moment show that  $S = 2$  is the ground state for high-spin mononuclear Mn<sup>3+</sup> in **5** at 20 °C. Application of the Bleaney–Bowers<sup>10</sup> equation permits evaluation of  $D$ ,  $|2J|$ , and an average  $g$  value for powder samples. Measurement of the ESR spectrum arising from **5** with the  $S = 2$  state and application of the spin Hamiltonian (eq 1) permits derivation of the rhombic ZFS parameter  $E$ .

## Experimental Section

**Preparation of Complex 2-NCH<sub>3</sub>NCTPP (**3**).** A solution of NCTPPH<sub>2</sub> (**4**) (0.5 g, 0.81 mmol) and CH<sub>3</sub>I (0.3 mL, 2.1 mmol) in dry *p*-xylene (10 mL) in the presence of dry Cs<sub>2</sub>CO<sub>3</sub> (0.5 g, 1.5 mmol) was heated for 2 h. After cooling down to room temperature (rt), the mixture was filtered and purified by column chromatographic separation with EtOAc–CH<sub>2</sub>Cl<sub>2</sub> [1:4 (v/v)] as a green band on silica gel (70–230 mesh, 60 g). Further recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–MeOH [1:2 (v/v)] afforded **3** (0.3 g, 0.47 mmol, 48.6%) as a blue solid.

**Sn(2-NCH<sub>3</sub>NCTPP)Cl<sub>2</sub> (**6**).** A mixture of 2-NCH<sub>3</sub>NCTPPH (**3**) (50 mg, 0.08 mmol) and SnCl<sub>2</sub> (300 mg, 1.6 mmol) was refluxed in pyridine (10 mL) for 30 min, poured into hexane (50 mL), and filtered, and the solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub>. The resulting CH<sub>2</sub>Cl<sub>2</sub> solution was rotary evaporated to dryness, and the residue was purified by a silica gel column using CH<sub>2</sub>Cl<sub>2</sub>/MeOH (2% MeOH) as the eluent, which on further recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH afforded **6** (40 mg, 0.053 mmol, 66%) as a blue solid. Compound **6** was redissolved in CH<sub>2</sub>Cl<sub>2</sub> and layered with MeOH to afford blue crystals for single-crystal X-ray analysis. <sup>1</sup>H NMR (599.95 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  8.98 [d, H <sub>$\beta$</sub> , <sup>3</sup>J(H–H) = 5.4 Hz]; 8.95 [d, H <sub>$\beta$</sub> , <sup>3</sup>J(H–H) = 4.8 Hz]; 8.86 [d, H <sub>$\beta$</sub> , <sup>3</sup>J(H–H) = 4.8 Hz]; 8.82 [d, H <sub>$\beta$</sub> , <sup>3</sup>J(H–H) = 4.2 Hz]; 8.81 [d, H <sub>$\beta$</sub> , <sup>3</sup>J(H–H) = 4.2 Hz]; 8.76 [d, H <sub>$\beta$</sub> , <sup>3</sup>J(H–H) = 4.2 Hz]; 8.22 [d, <sup>3</sup>J(H–H) = 4.2 Hz, *o*-H (*ortho* proton)] and 8.10 [d, <sup>3</sup>J(H–H) = 4.2 Hz, *o*-H]; 8.13 [d, <sup>3</sup>J(H–H) = 7.2 Hz, *o*-H] and 8.00 [d, <sup>3</sup>J(H–H) = 7.2 Hz, *o*-H]; 7.97 [d,

<sup>3</sup>J(H–H) = 7.2 Hz, *o*-H] and 7.61 [d, <sup>3</sup>J(H–H) = 7.2 Hz, *o*-H]; 7.47–7.78 [m, *meta* and *para* protons]; 3.30 (s, N-CH<sub>3</sub>). FAB-MS  $m/z$  (assignment, rel intensity): 154 ([NBA + H]<sup>+</sup>, 56.82), 761 ([Sn(4-NCH<sub>3</sub>NCTPP)]<sup>+</sup>, 48.11), 796 ([Sn(4-NCH<sub>3</sub>NCTPP)Cl]<sup>+</sup>, 100). UV–vis spectrum,  $\lambda$  (nm) [ $\epsilon \times 10^{-3}$ , M<sup>-1</sup> cm<sup>-1</sup>] in CH<sub>2</sub>Cl<sub>2</sub>: 458 (126.1), 565 (29.8), 606 (31.4), 722 (23.3), 884 (32.2).

**Mn(2-NCH<sub>3</sub>NCTPP)Br (**5**).** A mixture of 2-NCH<sub>3</sub>NCTPPH (**3**) (50 mg, 0.08 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and MnBr<sub>2</sub> (52 mg, 0.24 mmol) in MeOH (1 mL) was refluxed for 3 h. After concentrating it, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered. The filtrate was concentrated and the residue was purified by a silica gel column using CH<sub>2</sub>Cl<sub>2</sub>/EA [20% EA (ethyl acetate)] as the eluent to yield impure **5**, which upon further recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/EA afforded **5** (37 mg, 0.049 mmol, 61%) as a pure green solid. Compound **5** was redissolved in CH<sub>2</sub>Cl<sub>2</sub> and layered with EA to afford green crystals for single-crystal X-ray analysis. FAB-MS  $m/z$  (assignment, rel intensity): 629 ([4-NCH<sub>3</sub>NCTPP]<sup>+</sup>, 27.35), 681 ([Mn(4-NCH<sub>3</sub>NCTPP)]<sup>+</sup>, 100), 762 ([Mn(4-NCH<sub>3</sub>NCTPP)Br + H]<sup>+</sup>, 4.67). UV–vis spectrum,  $\lambda$  (nm) [ $\epsilon \times 10^{-3}$ , M<sup>-1</sup> cm<sup>-1</sup>] in CH<sub>2</sub>Cl<sub>2</sub>: 396 (35.9), 416 (34.1), 459 (24.6), 508 (59.3), 582 (10.7), 752 (10.1), 815 (12.7), 884 (12.3). Anal. Calcd. for C<sub>45</sub>H<sub>30</sub>BrMnN<sub>4</sub>: C, 70.90; H, 3.90; N, 7.30. Found: C, 70.49; H, 4.17; N, 7.22.

**Magnetic Susceptibility Measurements.** The solid-state magnetic susceptibilities were measured under helium on a Quantum Design MPMS5 SQUID susceptometer from 2 to 300 K at a field of 5 kG. The sample was held in a Kel-F bucket. The bucket had been calibrated independently at the same field and temperature. The raw data for **5** were corrected for the molecular diamagnetism. The diamagnetic contribution of the complex **5** was measured from an analogous diamagnetic metal complex, that is, **6**. The details of the diamagnetic corrections made can be found in ref 9.

**Spectroscopy.** ESR spectra were measured on an X-band Bruker EMX-10 spectrometer equipped with an Oxford Instruments liquid helium cryostat. Magnetic field values were measured with a digital counter. The X-band resonator was a dual-mode cavity (Bruker ER 4116 DM). <sup>1</sup>H NMR spectra were recorded at 599.95 MHz on a Varian Unity Inova-600 spectrometer using the solvent CDCl<sub>3</sub> and  $\delta = 7.24$  as the reference peak. Element analyses were carried out on an Elementar Vario EL III analyzer.

The positive-ion fast atom bombardment mass spectrum (FABMS) was obtained in a nitro benzyl alcohol (NBA) matrix using a JEOL JMS-SX/SX 102A mass spectrometer. UV–vis spectra were recorded at 20 °C on a Hitachi U-3210 spectrophotometer.

**Crystallography.** Table 1 presents the crystal data as well as other informations for **5** and **6**·2(0.2MeOH). Measurements were taken on a Bruker AXS SMART-1000 diffractometer using monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Empirical absorption corrections were made for both complexes. The structures were solved by direct methods (SHELXTL-97)<sup>11</sup> and refined by the full-matrix least-squares method. All non-hydrogen atoms were refined with anisotropic thermal parameters, whereas all hydrogen atoms were placed in calculated positions and refined with a riding model. The Br coordination to Mn(1) within **5** is disordered with an occupancy factor of 0.6 for Br(1) and 0.4 for Br(1'). These Br(1) and Br(1') atoms were also refined with anisotropic thermal parameters. Table 2 lists selected bond distances and angles for both complexes.

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**Table 1.** Crystal Data for **5** and **6**·2(0.2MeOH)

formula	C <sub>45.4</sub> H <sub>30</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>0.4</sub> Sn( <b>6</b> ·2(0.2MeOH))	C <sub>45</sub> H <sub>30</sub> N <sub>4</sub> MnBr ( <b>5</b> )
fw	827.52	761.58
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
cryst syst	monoclinic	monoclinic
<i>a</i> , Å	10.0782(10)	10.1225(18)
<i>b</i> , Å	8.3363(7)	16.506(3)
<i>c</i> , Å	23.747(2)	21.104(4)
α, deg	90	90
β, deg	95.061(2)	90.989(3)
γ, deg	90	90
<i>V</i> , Å <sup>3</sup>	1987.3(3)	3525.6(10)
<i>Z</i>	2	4
<i>F</i> <sub>000</sub>	835	1552
<i>D</i> <sub>calc</sub> , g cm <sup>-3</sup>	1.383	1.435
μ(Mo Kα), mm <sup>-1</sup>	0.815	1.547
<i>S</i>	1.106	1.075
cryst size, mm <sup>3</sup>	0.31 × 0.22 × 0.20	0.158 × 0.143 × 0.125
θ, deg	2.13 to 26.08	1.93 to 26.17
<i>T</i> , K	293(2)	293(2)
no. of reflns measd	3944	6976
no. of reflns obsd	3186	4555
<i>R</i> 1 <sup>a</sup> (%)	6.67	7.09
w <i>R</i> 2 <sup>b</sup> (%)	23.12	21.53

$$^a R1 = [\sum ||F_o| - |F_c||] / \sum |F_o|. \quad ^b wR2 = \{[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for Compounds **5** and **6**·2(0.2MeOH)

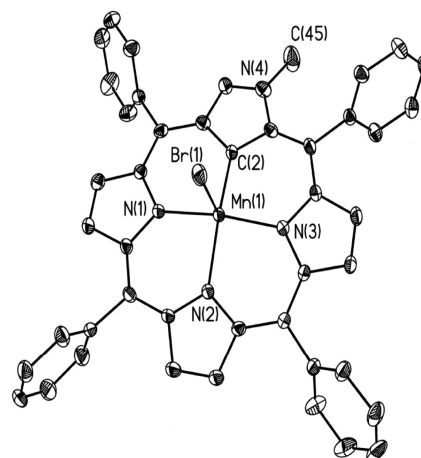
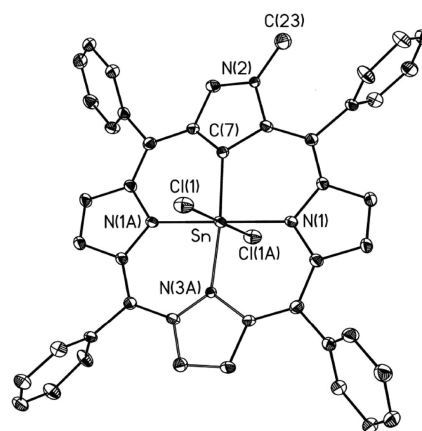
<b>5</b>			
Br(1)–Mn(1)	2.570(4)	Br(1')–Mn(1)	2.458(7)
Mn(1)–C(2)	2.008(5)	Mn(1)–N(1)	2.051(4)
Mn(1)–N(2)	2.047(4)	Mn(1)–N(3)	2.022(4)
H(45A)–Br(1)	2.982(4)	C(45)–Br(1)	3.907(4)
C(2)–Mn(1)–N(3)	87.95(18)	N(3)–Mn(1)–N(1)	160.98(18)
C(2)–Mn(1)–N(1)	88.07(17)	C(2)–Mn(1)–N(2)	161.79(19)
N(3)–Mn(1)–N(2)	89.42(16)	N(1)–Mn(1)–N(2)	88.58(16)
C(2)–Mn(1)–Br(1')	97.0(2)	N(3)–Mn(1)–Br(1')	96.20(17)
N(1)–Mn(1)–Br(1')	102.75(17)	N(2)–Mn(1)–Br(1')	101.18(19)
C(2)–Mn(1)–Br(1)	101.99(17)	N(3)–Mn(1)–Br(1)	103.72(14)
N(1)–Mn(1)–Br(1)	95.31(14)	N(2)–Mn(1)–Br(1)	96.14(15)
C(45)–H(45A)–Br(1)	162.17(14)		
<b>6</b> ·2(0.2MeOH)			
Sn–C(7)	2.063(19)	Sn–Cl(1)	2.5116(17)
Sn–N(1)	2.123(5)	Sn–N(3A)	2.084(14)
Cl(1)–Sn–Cl(1A)	180.00(8)	C(7)–Sn–N(1)	91.5(5)
Cl(1)–Sn–C(7)	88.6(5)	Cl(1)–Sn–N(1)	90.55(16)
C(7)–Sn–N(3A)	172.9(7)		

## Results and Discussion

**Molecular Structures of **5** and **6**·2(0.2MeOH).** Mn(2-NCH<sub>3</sub>NCTPP)Br (**5**) was produced in 61% yield by heating a 2-NCH<sub>3</sub>NCTPPH (**3**) solution in CH<sub>2</sub>Cl<sub>2</sub>/MeOH under aerobic conditions with an excess of MnBr<sub>2</sub> (Scheme 1).

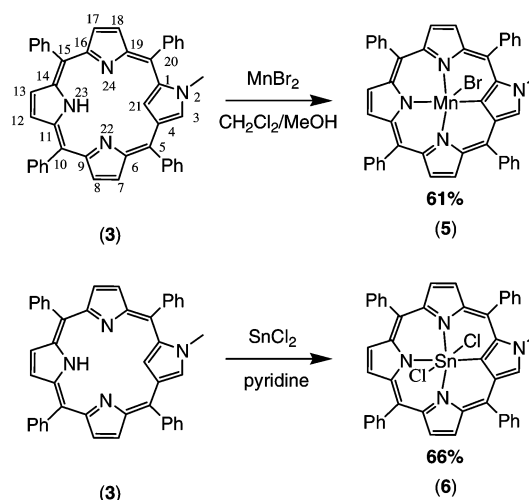
The complex Sn(2-NCH<sub>3</sub>NCTPP)Cl<sub>2</sub> (**6**) was synthesized in 66% yield by reacting 2-NCH<sub>3</sub>NCTPPH (**3**) with excess SnCl<sub>2</sub> in pyridine under aerobic conditions (Scheme 1). X-ray structures are depicted in Figure 1a for complex **5** and Figure 1b for **6**·2(0.2MeOH).

The geometry of the coordination around Mn(III) in **5** is closely related to a square-base pyramid, giving a trigonal distortion parameter ( $\tau$ ) value of 0.01, with Mn(III) having coordination of five, MnN<sub>3</sub>CBr, with normal bonds to the N(1), N(2), N(3), C(2), and Br(1) atoms. The bond lengths of Mn(1)–C(2), Mn(1)–N(1), Mn(1)–N(2), Mn(1)–N(3),

**(5)****(6)**

**Figure 1.** (a) Molecular structure of Mn(2-NCH<sub>3</sub>NCTPP)Br (**5**) and (b) Sn(2-NCH<sub>3</sub>NCTPP)Cl<sub>2</sub>·2(0.2MeOH); **6**·2(0.2MeOH)], with 30% thermal ellipsoids. Hydrogen atoms and solvent MeOH for **6**·2(0.2MeOH)] are omitted for clarity.

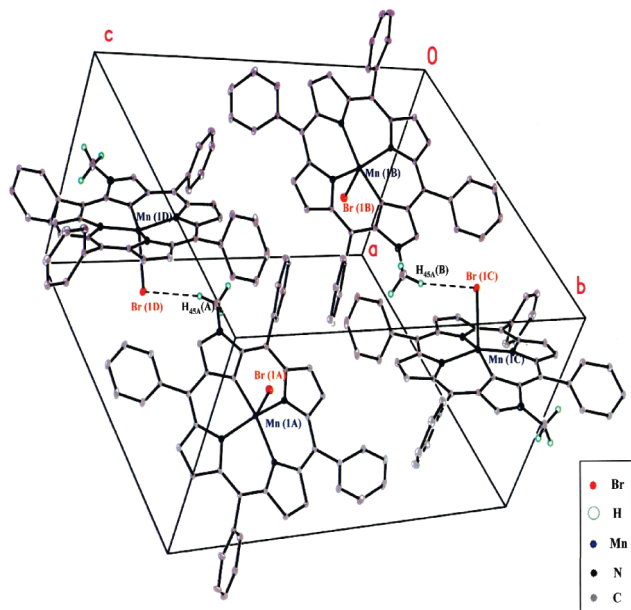
## Scheme 1



and Mn(1)–Br(1) in **5** are 2.008(5), 2.051(4), 2.047(4), 2.022(4), and 2.570(4) Å, respectively (Table 2).

In **6**·2(0.2MeOH), the geometry about Sn is a slightly distorted octahedron and has six-coordination with two axial





**Figure 2.** View of the one-dimensional network of **5** linked through weak hydrogen bonds in the unit cell.

chloride ligands; the bond distances are as follows: Sn–Cl(1) = 2.5116(17), Sn–C(7) = 2.063(19), Sn–N(1) = 2.123(5), and Sn–N(3A) = 2.084(14) Å (Table 2). The tin atom in **6**·2(0.2MeOH) is directly in the plane of the four internal core atoms, and the manganese in **5** lies 0.33 Å above the plane of the core atoms. The structure of **6**·2(0.2MeOH) is similar to that of the Sn<sup>4+</sup> complex of N-confused tetraphenylporphyrin Sn(NCTPP)Cl<sub>2</sub>.<sup>12</sup>

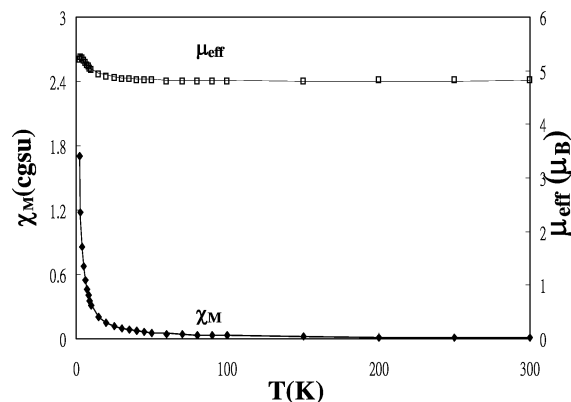
The crystal packing of complex **5** along the *b* axis is shown in Figure 2 in which weak hydrogen bonds link the mononuclear Mn(2-NCH<sub>3</sub>NCTPP)Br units into an extended one-dimensional chain.

The C(45)–H(45A)···Br(1) hydrogen bond is formed mainly between C(45) and Br(1) with a C(45)···Br(1) distance of 3.907(4) Å and a corresponding angle of 162.17(14)° (Table 2). The short interatomic contacts of H(45A)···Br(1) = 2.982(4) Å provide the most likely exchange pathway (Table 2).

**Spin Hamiltonian.** The quintet energy levels of the high-spin mononuclear Mn<sup>3+</sup> (*S* = 2) are parametrized in terms of the spin Hamiltonian<sup>13–15</sup>

$$(\hat{H}_s)_1 = D \left[ S_z^2 - \frac{1}{3} S(S+1) \right] + E(S_x^2 - S_y^2) + \beta H g S \quad (1)$$

where *H* is the applied magnetic field, *g* is the *g* tensor, *S* is the electronic spin, and *D* and *E* are the parameters which describe the effects of the axial and rhombic ligand field, respectively. The zero-field interaction splits the levels of system with *S* = 2 spin into two doublets, one of them is a linear combination of the *m<sub>s</sub>* = |±2⟩ states, that is, [|2<sup>+</sup>⟩, |2<sup>−</sup>⟩], and the other one of the *m<sub>s</sub>* = |±1⟩ states, that is, [|1<sup>+</sup>⟩,



**Figure 3.** Temperature variation of the molar magnetic susceptibility ( $\chi_M$ ) and effective magnetic moment ( $\mu_{\text{eff}}$ ) for the powder sample of **5** in the range 2–300 K. Points represent the experimental data; solid lines represent the least-squares fit of the data to eq 2.

|1<sup>−</sup>⟩], and a singlet corresponding to the *m<sub>s</sub>* = |0⟩ state, that is, |0'⟩.<sup>16</sup> The forbidden EPR transitions may be observed between the levels of the |2<sup>+</sup>⟩, |2<sup>−</sup>⟩ non-Kramer's doublet.<sup>1,16</sup>

**Magnetic Properties.** Magnetic data for complex **5** are reported in Figure 3 in the forms of  $\chi_M$  and  $\mu_{\text{eff}}$  versus *T*.

As can be seen in Figure 3, the  $\mu_{\text{eff}}$  for **5** remains constant at 4.83  $\mu_B$  from 300 K down to 30 K, below which it rises slowly to 5.25  $\mu_B$  at 3 K before decreasing again. This kind of behavior is expected for a high-spin mononuclear Mn(III) (*S* = 2) complex for **5** in which there is appreciable zero-field splitting of the ground state and/or weak ferromagnetic magnetic coupling. Low-symmetry *S* = 5/2 Mn(II) species, which may be present as impurities in Mn(III) compounds, can also give rise to downfield EPR signals near *g* = 2. The molecular structure of **5** shows that the metal (Mn) centers are linked by weak C(45)–H(45A)···Br(1) hydrogen bonds (Figure 2), and it is known that such interactions are able to transmit interactions. From a magnetic point of view, the weak one-dimensional arrangement of **5** may then be reduced to a dinuclear one.<sup>17</sup> The possibility of weak magnetic exchange in **5** with the spin Hamiltonian  $(\hat{H}_s)_2 = -2\bar{J}\bar{S}_1 \cdot \bar{S}_2 + \beta H g_s \cdot \bar{S}_t$  for Mn<sup>3+</sup>···Mn<sup>3+</sup> dimer (with *S*<sub>1</sub> = *S*<sub>2</sub> = 2) is included in fitting the magnetic susceptibility data.<sup>18</sup> Here  $\bar{S}_t$  is the total spin operator, that is, *S<sub>t</sub>* = 0, 1, 2, 3, 4 and *g<sub>s</sub>* = (*g*<sub>1</sub> + *g*<sub>2</sub>)/2.<sup>18</sup> The data were inserted into the Bleaney–Bowers equation (eq 2) and the term *p* (or *q*) which is the fraction of Mn<sup>3+</sup> (or Mn<sup>3+</sup>···Mn<sup>3+</sup> dimer), respectively,<sup>19,20</sup> where *y* = 1.44*D* (cm<sup>−1</sup>)/*T* and *x* = 1.44*J* (cm<sup>−1</sup>)/*T*. Here *g* is the average *g* value, TIP is the temperature independent paramagnetism, *p* (or *q*) is the fraction of Mn<sup>3+</sup> (or Mn<sup>3+</sup>···Mn<sup>3+</sup> dimer), and other symbols have their standard meanings. The best fits as represented in Figure 3 gave the values of *g* = 1.67, *D* = −2.4 cm<sup>−1</sup>, 2*J* = 1.12 cm<sup>−1</sup>, *p* = 0.56, *q* = 0.29, and a temperature independent paramagnetism value TIP

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$$\bar{\chi}_M = \frac{0.3749}{T} g^2 \left\{ p \cdot \frac{1}{3} \left[ \frac{8 + 2e^{3y} + \frac{1}{y} \left( -\frac{8}{3} - \frac{28}{3} e^{3y} + 12e^{4y} \right)}{2 + 2e^{3y} + e^{4y}} \right] \right. \\ \left. + q \left[ \frac{2e^{2x} + 10e^{6x} + 28e^{12x} + 60e^{20x}}{1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x}} \right] + (1 - p - q) \times 2.917 \right\} + TIP \quad \dots(2)$$

$\text{Mn}^{3+} \cdots \text{Mn}^{3+}(\text{dimer}) \quad \text{Mn}^{2+}(\text{impurity})$

$= 1.4 \times 10^{-4} \text{ cm}^3/\text{mol}$ . The negative value of  $-2J$  indicates a weak ferromagnetic nature of the spin coupling in  $\text{Mn}^{3+} \cdots \text{Mn}^{3+}(\text{dimer})$ . The intrachain  $\text{Mn} \cdots \text{Mn}$  separations of 9.558(4) Å in **5** precludes direct metal–metal bonding, so superexchange via the C(45)–H(45A)  $\cdots$  Br(1) hydrogen bonding in  $\text{Mn}^{3+} \cdots \text{Mn}^{3+}(\text{dimer})$  must be responsible for this ferromagnetic interaction (Figure 2). The shortest interchain  $\text{Mn} \cdots \text{Mn}$  distance of 11.508(4) Å indicates that the interchain interactions are expected to be negligible. This ferromagnetic interaction is quite weak, that is, similar to the previous result showing that coupling of Mn(III) ions with  $J = -0.2 \text{ cm}^{-1}$  in the complex (N-(2-hydroxybenzoyl)-N'-(2-hydroxybenzylidene)propane-1,2-diamine)-bis(methanol-O)-manganese(III),  $\text{L}^6\text{Mn}(\text{CH}_3\text{OH})_2$ , through  $\pi$ - $\pi$  stacking, although antiferromagnetic.<sup>17</sup>

**ESR Studies.** The X-band EPR spectra of a frozen solution of **5** in  $\text{CHCl}_3$  at 4 K is shown in Figure 4.

The field position and shape of the observed peak signal at  $g = 9.19$  (or 10.4) in parallel mode (or perpendicular mode) are close to those observed for tris(acetylacetonato)-manganese(III),  $\text{Mn}(\text{acac})_3$ , and are attributed to a forbidden transition within the  $|2^+\rangle$  and  $|2^-\rangle$  non-Kramer's doublet (Figure 4).<sup>1,16</sup> The resonance field for the transition between the  $\varepsilon|2^+\rangle$  and  $\varepsilon|2^-\rangle$  levels at a given  $h\nu$  quantum is calculated either from eq 3<sup>13,15</sup>

$$|\varepsilon|2^+\rangle - \varepsilon|2^-\rangle| = 2\sqrt{3}r \sin\left(\frac{\phi}{3} + 120^\circ\right) = h\nu \quad (3)$$

where  $r = [(4g^2\beta^2H^2)/3 + (16D^2)/9 + 4E^2]^{1/2}$ ,  $\cos\phi = (-q_1H^2 - q_2)/(2r^3)$ ,  $q_1 = (-32Dg^2\beta^2)/3$ , and  $q_2 = (128D^3)/27 + 16DE^2$ , or from eq 4<sup>14,16</sup>

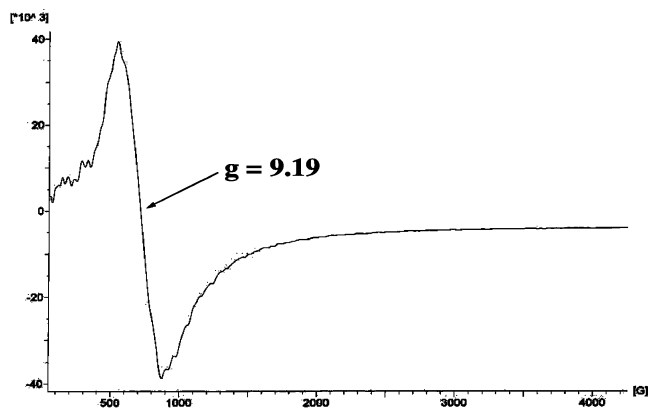
$$F_1H^6 + F_2H^4 + F_3H^2 + F_4 = 0 \quad (4)$$

where  $F_1 = 4p_1^3$ ,  $F_2 = 12p_1^2p_2 + 9p_1^2(h\nu)^2 + 27q_1^2$ ,  $F_3 = 12p_1p_2^2 + 18p_1p_2(h\nu)^2 + 6p_1(h\nu)^4 + 54q_1q_2$ ,  $F_4 = 4p_2^3 + 9p_2^2(h\nu)^2 + 6p_2(h\nu)^4 + (h\nu)^6 + 27q_2^2$ ,  $p_1 = -4g^2\beta^2$ , and  $p_2 = (-16D^2)/3 - 12E^2$ .

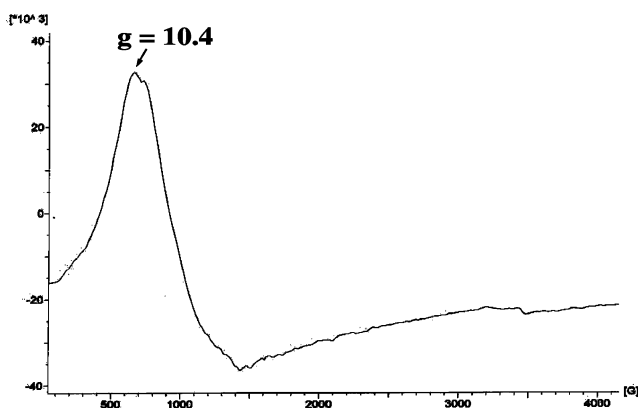
The rhombic zero field parameter  $E = -1.3 \times 10^{-3} \text{ cm}^{-1}$  is obtained by substitution of  $D = -2.4 \text{ cm}^{-1}$  and the field position of  $g = 9.19$  ( $H = 730.5 \text{ G}$ ) into either eq 3 or eq 4. Despite the lack of a  $C_4$  rotation axis, compound **5**, which is five-coordinate, shows relatively little rhombic ZFS. This ZFS is different from that of  $\text{Mn}(\text{NCTPP})(\text{py})_2$  (**2**), which is six-coordinate and has a relatively large magnitude, highly rhombic ZFS:  $D = -3.08 \text{ cm}^{-1}$ ,  $E = -0.61 \text{ cm}^{-1}$ .

## Conclusions

We have investigated two new inverted N-methyl porphyrin metal complex, namely, one paramagnetic **5** and one



(a)



(b)

**Figure 4.** X-band ESR spectra for **5** in  $\text{CHCl}_3$  at 4 K: (a) parallel polarization, (b) perpendicular polarization. ESR conditions: microwave frequency of 9.398 GHz (parallel polarization), 9.650 GHz (perpendicular polarization); microwave power of 3.994 mW, magnetic field modulation amplitude of 1.60 G, and modulation frequency of 100.00 KHz.

diamagnetic **6**, and their X-ray structures are established. A technique is also reported by combining the conventional ESR spectroscopy and magnetic susceptibility measurements to evaluate the ZFS parameters ( $D$  and  $E$ ) for the high-spin mononuclear Mn(III) ( $S = 2$ ) of **5**. The complex **5** is a mononuclear complex linked through H(45A)  $\cdots$  Br(1) hydrogen bonds into a one-dimensional chain and displays simple weak ferromagnetism between the Mn(III) ions.

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**Supporting Information Available:** The formula for non-Kramer's doublets, ORTEP drawings with the atom-labeling schemes for complexes **5** and **6**·2(0.2MeOH) (30% probability ellipsoids), and SQUID magnetic susceptibility for **5** in the temperature range of 2–100 K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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