

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,[†] Fuh-An Yang,[†] Jyh-Horung Chen,^{*,†} Shin-Shin Wang,[‡] and Jo-Yu Tung^{*,§}

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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 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 Cl^- ligands, whereas for the Mn^{3+} ion in **5**, it is a five-coordinate square pyramid (*SPY-5*) in which the unidentate 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 cm^{-1} and -0.0013 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 cm^{-1}); Q-band, $\sim 35 \text{ GHz}$ (1.2 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.^{1–3} 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.⁴ 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 Ziegler⁵ described the structural characterization of a six-coordinate Mn(III) complex of $\text{Mn}(\text{NCTPP})(\text{py})_2$ (**2**). Krzystek and co-workers⁶ 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.⁶

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- (1) Dexheimer, S. L.; Gohdes, J. W.; Chan, M. K.; Hagen, K. S.; Armstrong, W. H.; Klein, M. P. *J. Am. Chem. Soc.* **1989**, *111*, 8923.
- (2) Talsi, E. P.; Bryliakov, K. P. *Mendeleev Commun.* **2004**, 111.
- (3) Bryliakov, K. P.; Bahushkin, D. E.; Talsi, E. P. *Mendeleev Commun.* **1999**, 29.

(4) Bohle, D. S.; Chen, W. C.; Hung, C. H. *Inorg. Chem.* **2002**, *41*, 3334.

(5) Harvey, J. D.; Ziegler, C. J. *Chem. Commun.* **2003**, 2890.

(6) Harvey, J. D.; Ziegler, C. J.; Telser, J.; Ozarowski, A.; Krzystek, J. *Inorg. Chem.* **2005**, *44*, 4451.

Recently, Ziegler et al.⁷ reported an improved methodology for the synthesis of 2-N-methyl-5,10,15,20-tetraphenyl-21-carbaporphyrin, 2-NCH₃NCTPPH (**3**). Compound **3** in this work was prepared in the way described by the Ziegler group using CH₃I and *p*-xylene in 48.6% yield. Unlike the NH tautomerism that exists in NCTPPH₂ (**4**),⁸ 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-NCH₃NCTPP)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-NCH₃NCTPP)Cl₂; **6**]. This new diamagnetic compound **6** is used as a diamagnetic correction for **5** in the solid-state magnetic susceptibility measurements.⁹ 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 Mn³⁺ in **5** at 20 °C. Application of the Bleaney–Bowers¹⁰ 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-NCH₃NCTPP (3**).** A solution of NCTPPH₂ (**4**) (0.5 g, 0.81 mmol) and CH₃I (0.3 mL, 2.1 mmol) in dry *p*-xylene (10 mL) in the presence of dry Cs₂CO₃ (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–CH₂Cl₂ [1:4 (v/v)] as a green band on silica gel (70–230 mesh, 60 g). Further recrystallization from CH₂Cl₂–MeOH [1:2 (v/v)] afforded **3** (0.3 g, 0.47 mmol, 48.6%) as a blue solid.

Sn(2-NCH₃NCTPP)Cl₂ (6**).** A mixture of 2-NCH₃NCTPPH (**3**) (50 mg, 0.08 mmol) and SnCl₂ (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 CH₂Cl₂. The resulting CH₂Cl₂ solution was rotary evaporated to dryness, and the residue was purified by a silica gel column using CH₂Cl₂/MeOH (2% MeOH) as the eluent, which on further recrystallization from CH₂Cl₂/MeOH afforded **6** (40 mg, 0.053 mmol, 66%) as a blue solid. Compound **6** was redissolved in CH₂Cl₂ and layered with MeOH to afford blue crystals for single-crystal X-ray analysis. ¹H NMR (599.95 MHz, CDCl₃, 20 °C): δ 8.98 [d, H _{β} , ³J(H–H) = 5.4 Hz]; 8.95 [d, H _{β} , ³J(H–H) = 4.8 Hz]; 8.86 [d, H _{β} , ³J(H–H) = 4.8 Hz]; 8.82 [d, H _{β} , ³J(H–H) = 4.2 Hz]; 8.81 [d, H _{β} , ³J(H–H) = 4.2 Hz]; 8.76 [d, H _{β} , ³J(H–H) = 4.2 Hz]; 8.22 [d, ³J(H–H) = 4.2 Hz, *o*-H (*ortho* proton)] and 8.10 [d, ³J(H–H) = 4.2 Hz, *o*-H]; 8.13 [d, ³J(H–H) = 7.2 Hz, *o*-H] and 8.00 [d, ³J(H–H) = 7.2 Hz, *o*-H]; 7.97 [d,

³J(H–H) = 7.2 Hz, *o*-H] and 7.61 [d, ³J(H–H) = 7.2 Hz, *o*-H]; 7.47–7.78 [m, *meta* and *para* protons]; 3.30 (s, N-CH₃). FAB-MS m/z (assignment, rel intensity): 154 ([NBA + H]⁺, 56.82), 761 ([Sn(4-NCH₃NCTPP)]⁺, 48.11), 796 ([Sn(4-NCH₃NCTPP)Cl]⁺, 100). UV–vis spectrum, λ (nm) [$\epsilon \times 10^{-3}$, M⁻¹ cm⁻¹] in CH₂Cl₂: 458 (126.1), 565 (29.8), 606 (31.4), 722 (23.3), 884 (32.2).

Mn(2-NCH₃NCTPP)Br (5**).** A mixture of 2-NCH₃NCTPPH (**3**) (50 mg, 0.08 mmol) in CH₂Cl₂ (20 mL) and MnBr₂ (52 mg, 0.24 mmol) in MeOH (1 mL) was refluxed for 3 h. After concentrating it, the residue was dissolved in CH₂Cl₂ and filtered. The filtrate was concentrated and the residue was purified by a silica gel column using CH₂Cl₂/EA [20% EA (ethyl acetate)] as the eluent to yield impure **5**, which upon further recrystallization from CH₂Cl₂/EA afforded **5** (37 mg, 0.049 mmol, 61%) as a pure green solid. Compound **5** was redissolved in CH₂Cl₂ and layered with EA to afford green crystals for single-crystal X-ray analysis. FAB-MS m/z (assignment, rel intensity): 629 ([4-NCH₃NCTPP]⁺, 27.35), 681 ([Mn(4-NCH₃NCTPP)]⁺, 100), 762 ([Mn(4-NCH₃NCTPP)Br + H]⁺, 4.67). UV–vis spectrum, λ (nm) [$\epsilon \times 10^{-3}$, M⁻¹ cm⁻¹] in CH₂Cl₂: 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 C₄₅H₃₀BrMnN₄: 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). ¹H NMR spectra were recorded at 599.95 MHz on a Varian Unity Inova-600 spectrometer using the solvent CDCl₃ 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 α radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were made for both complexes. The structures were solved by direct methods (SHELXTL-97)¹¹ 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.

(7) Ou, W.; Ding, T.; Cetin, A.; Harvey, J. D.; Taschner, M. J.; Ziegler, C. J. *J. Org. Chem.* **2006**, *71*, 811.

(8) Chmielewski, P. J.; Latos-Grazynski, L. *J. Chem. Soc., Perkin Trans. 2* **1995**, 503.

(9) Drago, R. S. *Physical Methods for Chemists*, 2nd ed.; Saunders College Publishing: New York, 1992; pp 473–475, 591–593.

(10) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London.* **1952**, *A214*, 451.

(11) Sheldrick, G. M. *SHELXL-97. Program for Refinement of Crystal Structure from Diffraction Data*; University of Gottingen: Gottingen, Germany, 1997.

(12) Xie, Y.; Morimoto, T.; Furuta, H. *Angew. Chem., Int. Ed.* **2006**, *45*, 6907.

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

formula	C _{45.4} H ₃₀ Cl ₂ N ₄ O _{0.4} Sn(6 ·2(0.2MeOH))	C ₄₅ H ₃₀ N ₄ MnBr (5)
fw	827.52	761.58
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <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 ³	1987.3(3)	3525.6(10)
<i>Z</i>	2	4
<i>F</i> ₀₀₀	835	1552
<i>D</i> _{calc} , g cm ⁻³	1.383	1.435
μ(Mo Kα), mm ⁻¹	0.815	1.547
<i>S</i>	1.106	1.075
cryst size, mm ³	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 ^a (%)	6.67	7.09
w <i>R</i> 2 ^b (%)	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)

5			
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)		
6 ·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-NCH₃NCTPP)Br (**5**) was produced in 61% yield by heating a 2-NCH₃NCTPPH (**3**) solution in CH₂Cl₂/MeOH under aerobic conditions with an excess of MnBr₂ (Scheme 1).

The complex Sn(2-NCH₃NCTPP)Cl₂ (**6**) was synthesized in 66% yield by reacting 2-NCH₃NCTPPH (**3**) with excess SnCl₂ 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 (τ) value of 0.01, with Mn(III) having coordination of five, MnN₃CBr, 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),

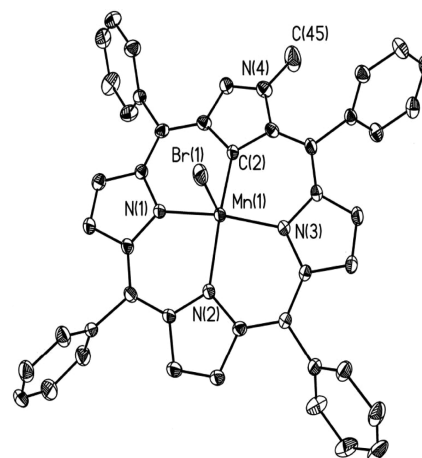
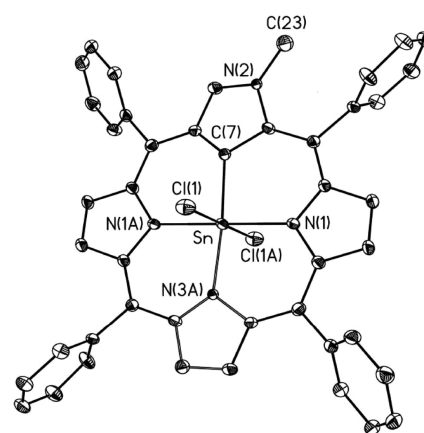
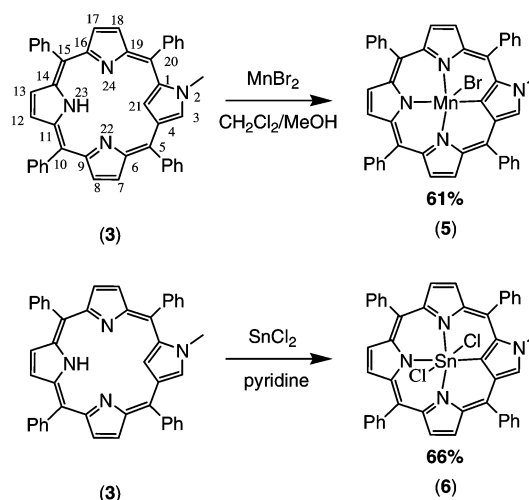
**(5)****(6)**

Figure 1. (a) Molecular structure of Mn(2-NCH₃NCTPP)Br (**5**) and (b) Sn(2-NCH₃NCTPP)Cl₂·2(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

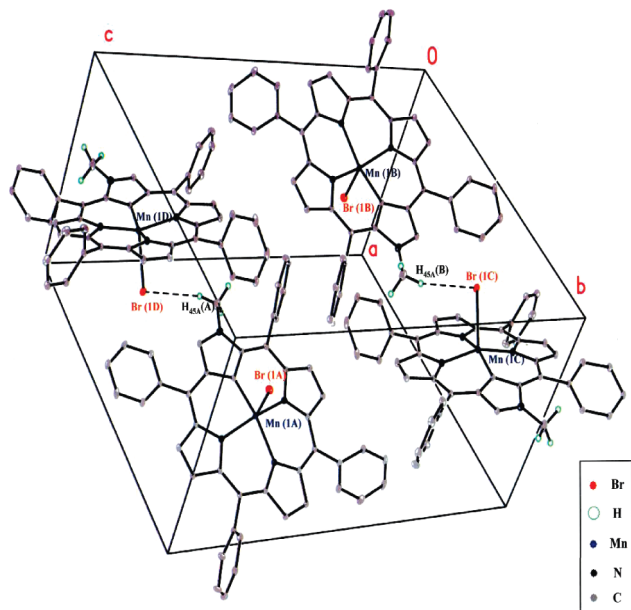


Figure 2. View of the one-dimensional network of **5** linked through weak hydrogen bonds in the unit cell.

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 Sn⁴⁺ complex of N-confused tetraphenylporphyrin Sn(NCTPP)Cl₂.¹²

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-NCH₃NCTPP)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 Mn³⁺ (*S* = 2) are parametrized in terms of the spin Hamiltonian^{13–15}

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

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_s* = |±2⟩ states, that is, [|2⁺⟩, |2[−]⟩], and the other one of the *m_s* = |±1⟩ states, that is, [|1⁺⟩,

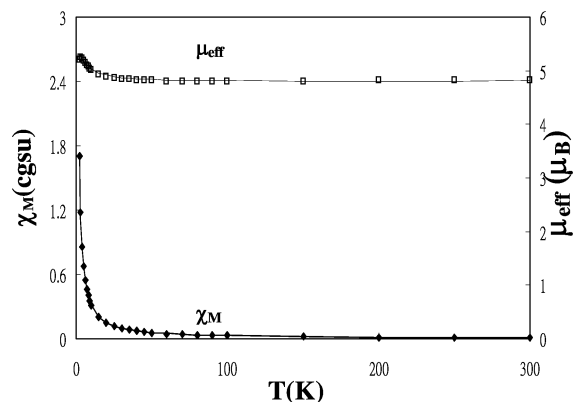


Figure 3. Temperature variation of the molar magnetic susceptibility (χ_M) and effective magnetic moment (μ_{eff}) for the powder sample of **5** in the range 2–300 K. Points represent the experimental data; solid lines represent the least-squares fit of the data to eq 2.

|1[−]⟩], and a singlet corresponding to the *m_s* = |0⟩ state, that is, |0'⟩.¹⁶ The forbidden EPR transitions may be observed between the levels of the |2⁺⟩, |2[−]⟩ non-Kramer's doublet.^{1,16}

Magnetic Properties. Magnetic data for complex **5** are reported in Figure 3 in the forms of χ_M and μ_{eff} versus *T*.

As can be seen in Figure 3, the μ_{eff} for **5** remains constant at 4.83 μ_B from 300 K down to 30 K, below which it rises slowly to 5.25 μ_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.¹⁷ 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 Mn³⁺···Mn³⁺ dimer (with *S*₁ = *S*₂ = 2) is included in fitting the magnetic susceptibility data.¹⁸ Here $\bar{S}_t$ is the total spin operator, that is, *S_t* = 0, 1, 2, 3, 4 and *g_s* = (*g*₁ + *g*₂)/2.¹⁸ The data were inserted into the Bleaney–Bowers equation (eq 2) and the term *p* (or *q*) which is the fraction of Mn³⁺ (or Mn³⁺···Mn³⁺ dimer), respectively,^{19,20} where *y* = 1.44*D* (cm^{−1})/*T* and *x* = 1.44*J* (cm^{−1})/*T*. Here *g* is the average *g* value, TIP is the temperature independent paramagnetism, *p* (or *q*) is the fraction of Mn³⁺ (or Mn³⁺···Mn³⁺ 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^{−1}, 2*J* = 1.12 cm^{−1}, *p* = 0.56, *q* = 0.29, and a temperature independent paramagnetism value TIP

(13) Gerritsen, H. J.; Sabisky, E. S. *Phys. Rev.* **1963**, *132*, 1507.

(14) Baranowski, J.; Cukierda, T.; Jezowska-Trzebiatowska, B.; Kozłowski, H. *J. Magn. Reson.* **1979**, *33*, 585.

(15) Hendrich, M. P.; Debrunner, P. G. *Biophys. J.* **1989**, *56*, 489.

(16) The formula for Non-Kramer's doublets are shown in the Supporting Information.

(17) Costes, J. P.; Dahan, F.; Donnadieu, B.; Douton, M. J. R.; Garcia, M. I. F.; Bousseksou, A.; Tuchagues, J. P. *Inorg. Chem.* **2004**, *43*, 2736.

(18) Yang, F. A.; Guo, C. W.; Chen, Y. J.; Chen, J. H.; Wang, S. S.; Tung, J. Y.; Hwang, L. P.; Elango, S. *Inorg. Chem.* **2007**, *46*, 578.

(19) Mathe, J.; Schinkel, C. J.; Amstel, W. A. V. *Chem. Phys. Lett.* **1975**, *33*, 528.

(20) Yates, M. L.; Arif, A. M.; Manson, J. L.; Kalm, B. A.; Barkhart, B. M.; Miller, J. S. *Inorg. Chem.* **1998**, *37*, 840.

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

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

$= 1.4 \times 10^{-4} \text{ cm}^3/\text{mol}$. 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 π - π stacking, although antiferromagnetic.¹⁷

ESR Studies. The X-band EPR spectra of a frozen solution of **5** in 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).^{1,16} 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^{13,15}

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

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^{14,16}

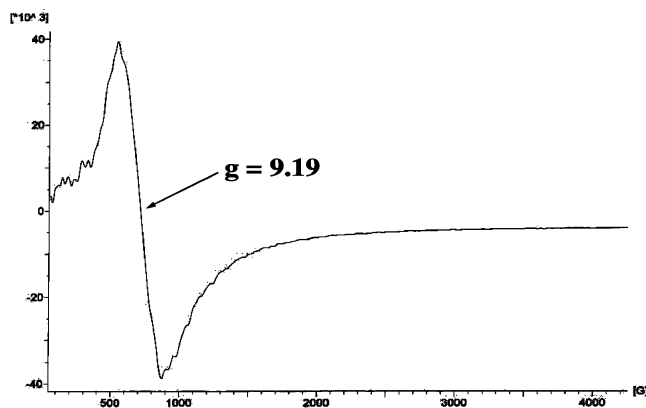
$$F_1H^6 + F_2H^4 + F_3H^2 + F_4 = 0 \quad (4)$$

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 $p_2 = (-16D^2)/3 - 12E^2$.

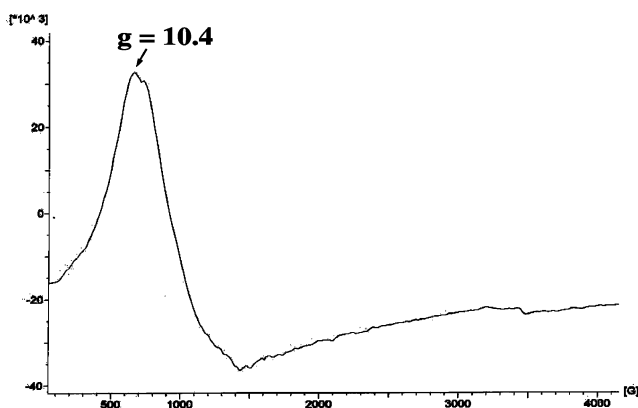
The rhombic zero field parameter $E = -1.3 \times 10^{-3} \text{ cm}^{-1}$ is obtained by substitution of $D = -2.4 \text{ cm}^{-1}$ and the field position of $g = 9.19$ ($H = 730.5 \text{ G}$) into either eq 3 or eq 4. Despite the lack of a C_4 rotation axis, compound **5**, which is five-coordinate, 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 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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