Inorg. Chem. **2006**, 45, 8847–8849

Inorganic Chemistry
Communication

Coexistence of Spin Canting and Metamagnetism in a One-Dimensional Mn(III) Complex Bridged by a Single End-to-End Azide

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Received July 28, 2006

Two manganese(III) azide complexes capped with tetradentate Schiff bases were characterized structurally and magnetically. The replacement of halogens on the Schiff bases leads to a drastic structural alteration from a dimer (**1**) bridged by phenoxide to a one-dimensional chain (**2**) linked by azide in a single end-to-end mode. Notably, magnetic studies of **2** show the concomitant existence of spin canting and metamagnetism.

Molecule-based magnetic materials have been one of the current issues because of the emergence of new intriguing physical properties in low-dimensional magnetic systems such as single-molecule magnets and single-chain magnets.[1] To achieve such magnetic entities the reasonable choice of proper bridging ligands is of ultimate importance because they can communicate magnetic couplings between paramagnetic metal ions and then determine the magnetic strength and nature. Along these lines, azide is an excellent ligand in terms of constructing diverse structural topologies from discrete molecules to three-dimensional networks and predicting the magnetic nature depending on the binding mode.[2] In general, the end-on mode gives ferromagnetic interaction and the end-to-end mode produces antiferromagnetic coupling with exceptional examples.[3] The magnetic interactions in azide-bridged complexes, coupled with a degree of magnetic anisotropy, result in some basic events involving spin flop,[4] spin canting,[3a,b] and metamagnetism.[5] The individual properties in multidimensional magnetic materials based on azide bridges are often revealed and well characterized from a magnetostructural point of view.[3−5] However, studies on the blended magnetic features simultaneously exhibiting spin canting/spin flop or spin canting/metamagnetism are still rare.[6]

To fabricate low-dimensional aggregates including magnetic anisotropy, the adoption of Mn(III) precursors with tetradentate Schiff bases (SBs) would be appropriate because the SB coligands enable one to stabilize the oxidation state of Mn(III) that is composed of single-ion anisotropy. A few azide-bridged Mn(III) compounds chelated with tetradentate SB ligands have been reported displaying mainly antiferromagntic interactions through end-to-end azide linkage.[7] To the best of our knowledge, the presence of the dual magnetic characters has not yet been shown for azide-bridged Mn(III) systems.

Herein we report the synthesis, crystal structures, and magnetic properties of a dinuclear complex $[\mathrm{Mn(5\text{-}Clsalen)(N_3)}]_2$ (**1**) with phenoxide bridges and a one-dimensional chain $[\mathrm{Mn(5\text{-}Brsalen)(N_3)}]_n$ (**2**) linked by azide in a single end-to-end fashion. It is worth noting that spin canting and metamagnetism coexist in **2**, which is a unique example of the one-dimensional Mn(III) systems connected by end-to-end azide ligands.

A stoichiometric reaction of $[\mathrm{Mn(SB)(H_2O)}](\mathrm{ClO_4})$ (SB = 5-Clsalen and 5-Brsalen) and $\mathrm{NaN_3}$ in MeOH ($T = 70{-}80$ °C) for 24 h produced red-brown crystals in yields of 25% (**1**) and 42% (**2**).[8] The strong IR absorptions are observed at 2039vs and 2027vs (sh) cm^{-1} for **1** and 2024vs and 2016vs (sh) cm^{-1} for **2**, attributed to the asymmetric stretching frequencies of the azide ligands.

An ORTEP diagram of **1** showing the atom-labeling scheme is illustrated in Figure 1a. The Mn center has a

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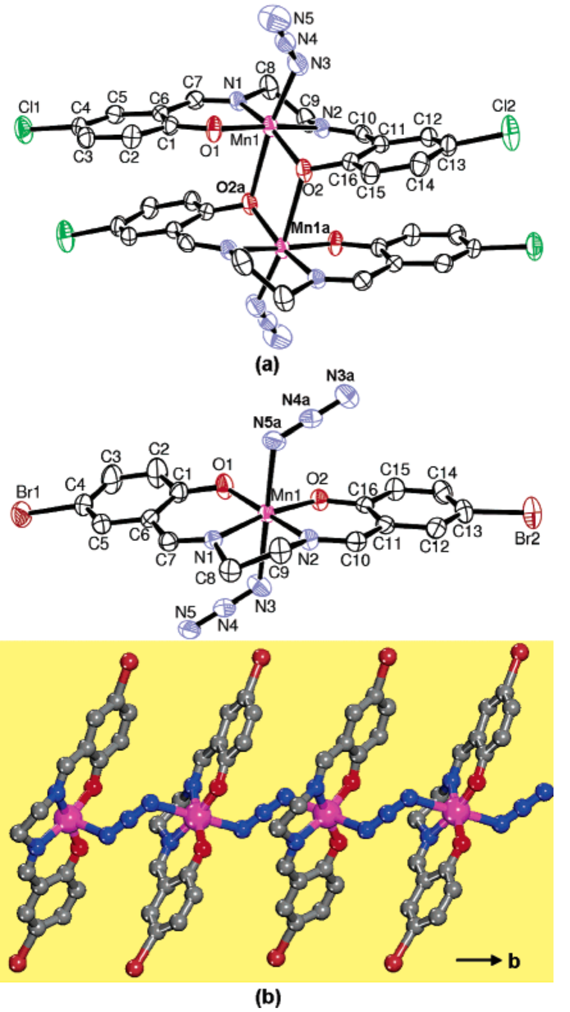

Figure 1. Molecular structures of (a) **1** with a symmetry code of $a = 2 - x, -y, 1 - z$ and (b) **2** with a symmetry code of $a = 1.5 - x, 0.5 + y, z$. The chain is running along the *b* axis.

distorted octahedral arrangement consisting of three O atoms from 5-Clsalen and three N atoms from 5-Clsalen and azide, and a significant tetragonal elongation around the Mn(III) ion occurs as a result of the Jahn–Teller effect. The equatorial N_2O_2 plane originating from 5-Clsalen exhibits an average Mn–N(O) distance of 1.93(6) Å, while the remaining two axial sites are separated from Mn1 with 2.120(3) Å for Mn1–N3 and 2.6706(19) Å for Mn1–O2a ($a = 2 - x, -y, 1 - z$). The angle of Mn1–O2–Mn1a is 99.93(7)°. The shortest intra- and interdimer Mn–Mn distances are 3.5390(6) and 8.2080(8) Å, respectively. A notable structural peculiarity in **1** is that the benzene rings from two adjacent 5-Clsalen in the dimer are not planar, forming a dihedral angle of 7.8(2)°. This indicates that the Cl atoms on the two rings are repelled against each other and separated by 3.8857(14) Å, which is longer than the van der Waals radii (3.5 Å). Strikingly, the use of 5-Brsalen instead of 5-Clsalen allows for the obvious structural alteration from the dimer (**1**) to a one-dimensional chain (**2**) as seen in Figure 1b, which may be due to a steric hindrance caused by the bulkier Br atoms. A tetragonally distorted Mn center is surrounded by two O atoms and two N atoms from 5-Brsalen, forming the equatorial N_2O_2 plane [ave Mn–N(O) = 1.93(6) Å], and two apical N atoms from bridging azides [Mn1–N3 = 2.341(3) Å, Mn1–N5a = 2.299(3) Å; $a = 1.5 - x, 0.5 + y, z$]. The azide ligand links two Mn atoms in a single end-to-end mode with a mean angle of 119.3(4)° for Mn–N–N(azide). It is noticed that the nearest N_2O_2 basal planes along the chain are substantially tilted at a dihedral angle of 61.42(7)°, providing crystallographically different Mn(III) environments. The shortest intra- and interchain Mn–Mn and interchain Br–Br distances are 5.6343(6), 7.0630(8), and 3.9685(7) Å, respectively (Figure S1 in the Supporting Information).

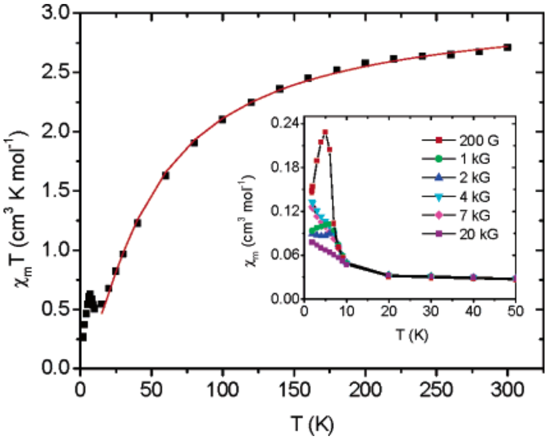

Figure 2. Plot of $\chi_m T$ vs T for **2**. The solid line shows the best theoretical fit. The inset presents the χ_m vs T plots at various fields.

The magnetic susceptibility of **1**, shown in Figure S2 in the Supporting Information, was measured at 0.1 T in the temperature range 1.8–300 K. Upon cooling, the $\chi_m T$ value of 6.09 cm^3 K mol^{-1} at 300 K goes on a slow rise and then rapidly increases at low temperatures, reaching a value of 9.38 cm^3 K mol^{-1} at 1.8 K. This implies the presence of ferromagnetic interactions between Mn(III) ions through the phenoxide routes. The calculated magnetic parameters are estimated to be $g = 2.01$, $J = 0.42$ cm^{-1}, and $D \approx 0$ on the basis of the $H = -JS_{\mathrm{Mn1}} \cdot S_{\mathrm{Mn1a}}$ scheme using the *MAGPACK* program,[9] which falls into the normal range of phenoxide-bridged Mn(III) dimers.[10]

Figure 2 shows the temperature dependence of magnetic susceptibility data of **2**. The $\chi_m T$ value of 2.71 cm^3 K mol^{-1} at 300 K is slightly smaller than that expected for a noninteracting Mn(III) ion. As the temperature is lowered, $\chi_m T$ undergoes a gradual decrease down to 0.51 cm^3 K mol^{-1} at 10 K, indicating antiferromagnetic couplings within a

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(8) Anal. Calcd for **1**: C, 44.5; H, 2.80; N, 16.2. Found: C, 44.3; H, 2.70; N, 16.1. Crystal data for **1**: $C_{32}H_{24}Cl_4Mn_2N_{10}O_4$, $M = 864.3$, monoclinic, $P2_1/n$, $a = 8.6518(4)$ Å, $b = 14.9198(7)$ Å, $c = 13.5957(7)$ Å, $\beta = 107.366(3)°$, $V = 1674.98(14)$ Å^3, $Z = 2$, $D_c = 1.714$ g cm^{-3}, $F(000) = 872$. Final R indices were R1 = 0.0498 and wR2 = 0.0874 [$I > 2\sigma(I)$]. Anal. Calcd for **2**: C, 37.0; H, 1.94; N, 13.5. Found: C, 36.8; H, 2.35; N, 13.1. Crystal data for **2**: $C_{16}H_{12}Br_2MnN_5O_2$, $M = 521.07$, orthorhombic, *Pbca*, $a = 11.5082(2)$ Å, $b = 11.2664(2)$ Å, $c = 27.3565(5)$ Å, $V = 3546.93(11)$ Å^3, $Z = 8$, $D_c = 1.952$ g cm^{-3}, $F(000) = 2032$. Final R indices were R1 = 0.0387 and wR2 = 0.0766 [$I > 2\sigma(I)$].

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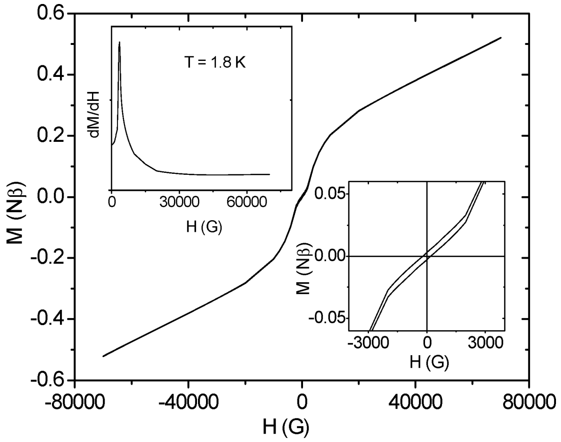

Figure 3. Field dependence of the magnetization of **2**. The insets give the derivative of *M* vs *H* and a blow-up of the hysteresis loop.

chain. Below 10 K, the $\chi_m T$ product experiences an upturn, arriving at a maximum at 7 K, and then finally decreases to 0.27 cm^3 K mol^{-1} at 2 K. This low-temperature behavior suggests the occurrence of a typical spin canting. The observation of the spin canting may arise from the presence of the two slanted basal planes of Mn(III) ions with single-ion anisotropy.[11] The cryomagnetic behavior of **2** obeys the Curie−Weiss law in the high-temperature region 100−300 K, yielding $C = 3.11$ cm^3 K mol^{-1} and $\theta = -43.2$ K. The magnetic data above 15 K can be analyzed using an infinite-chain model derived by Fisher ($H = -J\sum_i S_{Ai} \cdot S_{Ai+1}$) under consideration of a molecular-field approximation (zJ').[7,12] A best fit gives parameters of $g = 2.03$, $J = -6.5$ cm^{-1}, and $zJ' = -0.59$ cm^{-1}. The negative J value demonstrates that Mn(III) spins bridged by an end-to-end azide in a chain are coupled antiferromagnetically, which is consistent with azide-bridged Mn(III) systems.[7]

The low-temperature magnetic phenomena ($T < 15$ K) for **2** were scrutinized by applying various magnetic fields, as depicted in the inset of Figure 2. The peaks in χ_m vs T plots are observed in fields below 2 kG and disappear above 4 kG. These appealing phenomena are definitely associated with the canting behavior, which is confirmed by the $M(H)$ data in Figure 3, where the inflection point in $M(H)$ (inset of Figure 3) is found at $H_C = 3400$ G. The phase transition at H_C is also ascertained by the $\chi_{ac}(H)$ plot, in which a sharp peak is present at the same field (Figure S3 in the Supporting Information). Accordingly, the weak interchain antiferromagnetic interaction (zJ') is overcome by external magnetic fields above H_C, inducing an ordered weak ferromagnetic phase. There exists a divergence of zero-field-cooled (ZFCM) and field-cooled (FCM) magnetizations at 20 G, displaying the onset of a magnetized state at a critical temperature (T_C) of 6 K (Figure S4 in the Supporting Information). The critical temperature can be manifested by ac magnetic susceptibilities where maxima in χ_m' and χ_m'' occur at ca. 6 K, indicative of a long-range magnetic ordering (Figure S5 in the Supporting Information).[13] The hysteresis loop in the inset of Figure 3 denotes a coercive field of 200 G and a remnant magnetization of 0.0028 Nβ. Extrapolation of the high-field linear section of the magnetization to zero field affords a value of 0.137 Nβ, and the canting angle corresponds to 1.9°.[14]

In summary, we have prepared two Mn(III) complexes with the tetradentate SBs. The subtle variation of the side group from Cl to Br on the SB affects the overall molecular structures from the dimer (**1**) bridged by the phenoxide to the one-dimensional chain (**2**) in a single end-to-end mode. It is noted that compound **2** exhibits the coexistence of spin canting and metamagnetism, marking a rare example among the azide-bridged one-dimensional systems.

Acknowledgment. This work was supported by a Korea Research Foundation grant funded by the Korea Government (MOEHRD, Basic Research Promotion Fund; Grant KRF-2005-070-C00068) and CRM-KOSEF. C.S.H thanks an Operation Program on Shared Research Equipment of KBSI and MOST.

Supporting Information Available: Additional structural and magnetic data for **1** and **2** and X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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