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Weak Ferromagnetism in a Three-Dimensional Manganese(II) Azido Complex, $[Mn(4,4'\text{-bipy})(N_3)_2]_n$ (bipy = Bipyridine)

Sujin Han,[†] Jamie L. Manson,[‡,§] Jinkwon Kim,[*,†] and Joel S. Miller[*,‡]

Department of Chemistry, Kongju National University, 182 Shinkwan, Chungnam 314-701, Korea, and Department of Chemistry, University of Utah, 315 South 1400 East RM 2124, Salt Lake City, Utah 84112-0850

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Introduction

Several families of molecular materials exhibiting spontaneous magnetization below a critical temperature (T_c) have been discovered in the past several years.[1] The design of high-T_c ferromagnetic materials has been realized by organizing transition metal ions into three-dimensional networks by use of organic bridging ligands such as cyanide and tetracyanoethenide $[TCNE]^{\bullet -}$.[2,3] Another intriguing synthetic approach to molecular magnets utilizes azide (N_3^-) as a bridging ligand, due to its coordinative versatility in bridging two transition metal ions.[4] Magneto-structural correlations for azido-based magnetic materials have shown that the end-to-end (EE) bridging mode predominantly leads to antiferromagnetic coupling, and the end-on (EO) mode to ferromagnetic coupling.[4] Examples include dinuclear,[5] triangular,[6] tetragonal,[7] 1-D,[8] and 2-D[9] nickel(II) compounds.

In an effort to assemble high-dimensional compounds with a greater local spin to enhance the magnetic ordering temperatures, the Mn(II)−azido system has been examined extensively. Escuer and co-workers systematically studied several $[MnL_2(N_3)_2]_n$ compounds: 3-D for L = pyridine[10] and 2-D for L = 3-[11] and 4-acetylpyridine,[12] methyl-[13] and ethylisonicotinate,[10] and 4-cyanopyridine.[11] Others have also reported high-dimensional complexes by use of ancillary multidentate ligands such as bipyrimidine (2-D, EO),[14] pyrazine (2-D, EO),[15]1,2-bis(4-pyridyl)ethane (2-D, EE),[16] and 4,4′-bipyridine (3-D, EE)[17] as opposed to monodentate ligands, which promotes additional binding of the metal ions. Composed solely of azido 1,3-bridging units, $[NMe_4][Mn^{II}(N_3)_3]$ was found to possess a distorted perovskite-like structure.[18] Recent examples, $[Ni(5\text{-methylpyrazole})_4(N_3)][ClO_4]$[8] and $[Mn(4\text{-acpy})_2(N_3)_2]_n$ (acpy = acetylpyridine),[11] are weak ferromagnets, whereas all other EE-bonded materials show only antiferromagnetic coupling without a spontaneous moment.

A recent communication by Shen et al. reported the synthesis, crystal structure, and preliminary magnetic properties of $[Mn(4,4'\text{-bipyridine})(N_3)_2]_n$, **1**.[17] Their magnetic data suggested that **1** did not magnetically order down to 4 K and that only weak antiferromagnetic coupling was present. We found this particularly striking in that many of the known Mn(II)−azido complexes do show interesting magnetic behavior well above 4 K. As part of our studies on transition metal−azido complexes,[15] we reexamined the magnetic properties of 3-D $Mn(4,4'\text{-bipyridine})(N_3)_2]_n$, **1**, using detailed magnetic susceptibility and magnetization measurements, and we clearly observe weak ferromagnetism below T_c = 42.5 K, contrary to a previous report.[17] This work emphasizes the importance of taking low-field magnetic data to characterize the magnetic behavior of materials.

Experimental Section

$Mn(ClO_4)_2 \cdot 6H_2O$, 4,4′-bipyridine, and NaN_3 were uses as purchased (Aldrich). Infrared spectra (400−4000 cm^{-1}) were recorded on a Perkin-Elmer Spectrum 1000 FT-IR spectrometer with samples prepared as KBr pellets. C, H, and N elemental analysis were performed on an Elemental Anaylsen systeme GmbH Vario EL. Magnetic measurements were taken on a Quantum Design MPMS-5T magnetometer as previously described.[19]

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[*] Authors to whom correspondence should be addressed. E-mail: jkim@knu.kongju.ac.kr (J.K.); jsmiller@chemistry.utah.edu (J.S.M.).

[†] Kongju National University.

[‡] University of Utah.

[§] Present address: Chemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, IL 60439.

(1) E.g.: Miller, J. S.; Epstein, A. J. *Angew. Chem.* **1994**, *33*, 385. Miller, J. S.; Epstein, A. J. *Chem. Eng. News*, **1995**, *73*(40), 30. Kinoshita, M. *Jpn. J. Appl. Phys.* **1994**, *33*, 5718. Gatteschi, D. *Adv. Mater.* **1994**, *6*, 635. *Magnetic Molecular Materials*; D. Gatteschi, D., Kahn. O., Miller, J. S., Palacio, Eds.; F. NATO ASI Series 198; Kluwer: Dordrecht, 1991. *Magnetism: A Supramolecular Function*; Kahn, O., Ed.; NATO ASI Series; Kluwer: Dordrecht, 1996.

(2) (a) Ferlay, S.; Mallah, T.; Quahas, R.; Veillet, P.; Verdaguer, M. *Nature* **1995**, *378*, 701. (b) Hatlevik, Ø.; Buschmann, W. E.; Zhang, J.; Manson, J. L.; Miller, J. S. *Adv. Mater.* **1999**, *11*, 914. (c) Holmes, S. D.; Girolami, G. *J. Am. Chem. Soc.* **1999**, *121*, 5593.

(3) (a) Manriquez, J. M.; Yee, G. T.; McLean, R. S.; Epstein, A. J.; Miller, J. S. *Science* **1991**, *252*, 1415. Miller, J. S.; Yee, G. T.; Manriquez, J. M.; Epstein, A. J. In *Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structure*; Proceedings of Nobel Symposium NS-81; Oxford University Press: Oxford, 1993; pp 461. (b) Zhang, J.; Zhou, P.; Brinckerhoff, W. B.; Epstein, A. J.; Vazquez, C.; McLean, R. S. Miller, J. S. *ACS Symp. Ser.* **1996**, *644*, 311.

(4) Cortés, R.; Lezama, L.; Mautner, F. A.; Rojo, T. In *Molecule-Based Magnetic Materials*; Turnbull, M. M., Sugimoto, T., Thomson, L. K., Eds.; American Chemical Society: Washington, DC, 1996; pp 187−200.

(5) (a) Ribas, J.; Monfort, M.; Diaz, C.; Bastos, C.; Solans, X. *Inorg. Chem.* **1993**, *32*, 3557. (b) Vicente, R.; Escuer, A.; Ribas, J.; El Fallah, M. S.; Solans, X.; Font-Bardia, M. *Inorg. Chem.* **1993**, *32*, 1920.

(6) Escuer, A.; Castro, I.; Mautner, F.; El Fallah, M. S.; Vicente, R. *Inorg. Chem.* **1997**, *36*, 4633.

(7) Ribas, J.; Monfort, M.; Costa, R.; Solans, X. *Inorg. Chem.* **1993**, *32*, 695.

(8) Hong, C. S.; Do, Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 193.

(9) Ribas, J.; Monfort, M.; Solans, X.; Drillon, M. *Inorg. Chem.* **1994**, *33*, 742.

(10) Escuer, A.; Vicente, R.; Goher, M. A. S.; Mautner, F. A. *Inorg. Chem.* **1996**, *35*, 6386.

(11) Escuer, A.; Vicente, R.; Mautner, F. A.; Goher, M. A. S. *Inorg. Chem.* **1997**, *36*, 3440.

(12) Escuer, A.; Vicente, R.; Goher, M. A. S.; Mautner, F. A. *Inorg. Chem.* **1995**, *34*, 5707.

(13) Escuer, A.; Vicente, R.; Goher, M. A. S.; Mautner, F. A. *J. Chem. Soc., Dalton Trans.* **1997**, 4431.

(14) (a) Cortés, R.; Urtiaga, M. K.; Lezama, L.; Pizarro, J. L.; Arriortua, M. I.; Rojo, T. *Inorg. Chem.* **1997**, *36*, 5016. (b) Cortés, R.; Lezama, L.; Pizarro, J. L.; Arriortua, M. I.; Rojo, T. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1810.

(15) Manson, J. L.; Arif, A. M.; Miller, J. S. *Chem. Commun. (Cambridge)* **1999**, 1479.

(16) Hong, C. S.; Son, S.-G.; Lee, Y. S.; Jun, M.-J.; Do, Y. *Inorg. Chem.* **1999**, *38*, 5602.

(17) Shen, H.-Y.; Liao, D.-Z.; Jiang, Z.-H.; Yan, S.-P.; Sun, B.-W.; Wang, G.-L.; Yao, X.-K.; Wang, H.-G. *Chem. Lett.* **1998**, 469. The only reported magnetic data were the $\chi T(T)$ data measured at 4 and 296 K; neither the field at which the data was taken nor the θ value from a fit to the Curie−Weiss equation was reported. The room temperature χT value of 4.27 emu K/mol is substantially greater than the value reported herein.

(18) Mautner, F. A.; Cortés, R.; Lezama, L.; Rojo, T. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 78.

10.1021/ic000307z CCC: $19.00

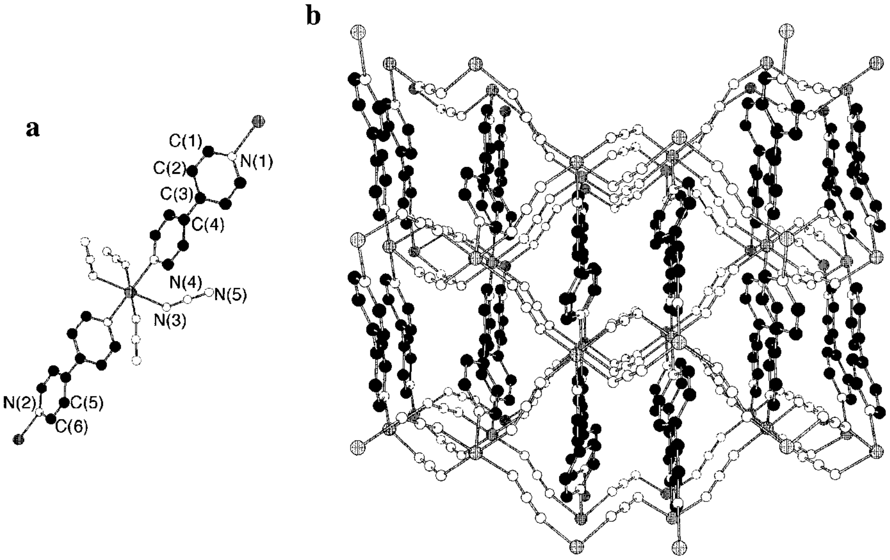

Figure 1. (a) Molecular structure of **1** showing only the Mn^{II} coordination sphere and atom-labeling scheme. (b) Perspective view of the crystal structure of $Mn(4,4'\text{-bipy})(N_3)_2$, **1**. Shaded, open, and filled spheres represent Mn, N, and C atoms, respectively.

$[Mn(4,4'\text{-bipyridine})(N_3)_2]_n$, 1, was prepared in a way similar to that described in ref 17, by mixing solutions of $Mn(ClO_4)_2 \cdot 6H_2O$, 4,4′-bipyridine, and NaN_3 in methanol (61% yield). Single crystals suitable for X-ray diffraction study were obtained from slow addition of sodium azide in methanol with a syringe pump during 3 days into the methanol solution of manganese perchlorate and 4,4-bipyridine. Anal. Calcd for $C_{10}H_8MnN_8$: C, 40.69; H, 2.73; N, 37.96. Found: C, 40.32; H, 2.71; N, 37.8. IR (KBr, cm^{-1}): ν(C−H), 3059 (w); $\nu_{as}(N_3)$, 2076 (vs); $\nu_s(N_3)$, 1323 (vw); ν(4,4′-bipy), 1601 (s), 1411 (s), 815 (s). To verify that **1** was identical to that reported earlier,[17] we redetermined the structure; space group = $P4_12_12$ (No. 92), $M = 295.18$, $a = 8.236(1)$ Å, $c = 16.937(3)$ Å, $V = 1148.8(3)$ Å^3, $Z = 4$, ρ(calcd) = 1.707 g cm^{-3}, R1= 0.0309, wR2 = 0.0687.

Results and Discussion

In light of our findings (vide infra), we verified the crystal structure[17] of **1** as it is relevant to the interpretation of the observed magnetic behavior. The molecular structure of **1** showing the coordination environment of the Mn^{2+} ion is given in Figure 1a, which has slightly elongated octahedral Mn^{II} centers composed of four EE-bonded N_3^- ligands, and two *trans*-coordinated 4,4′-bipyridine molecules. When extended in 3-D, an unprecedented network structure is formed, Figure 1b. The IR spectrum shows a very strong band at 2076 cm^{-1} for the $\nu_{asym}(N_3)$ mode, which is consistent with a structure containing an end-to-end bridging ligand. The azide symmetric stretch, $\nu_{sym}(N_3)$, is not active for the symmetrical EE coordination mode. However, **1** has a very weak $\nu_{sym}(N_3)$ band at 1323 cm^{-1} due to asymmetry of the EE bridges in the complex. A similar result was observed in the $[Ni(2,2'\text{-bipy})_2(N_3)]_n(ClO_4)_n$ chain complex.[21]

We verified the crystal structure of **1**,[17] which has slightly elongated octahedral Mn^{II} centers composed of four EE-bonded N_3^- ligands, and two *trans*-coordinated 4,4′-bipyridine molecules, which, when extended in 3-D, afford an unprecedented network structure, Figure 1. The tetragonal symmetry ($P4_12_12$) of the complex precludes a center of inversion. A variety of channel sizes and shapes are produced including triangular, rectangular, and hexagonal. Interestingly, solvent molecules do not intercalate into the cavities nor does a second interpenetrating network form. The 4,4′-bipyridine ligands are not coplanar but are twisted about the C−C bond by 31.9(2)°, and the Mn−N_{bipy} bond distances are inequivalent [2.256(4) and 2.304(4) Å]. The two kinds of Mn−N_{azide} bond distances are also different from each other [2.188(4) and 2.208(4) Å], which is consistent with the observation of the symmetric stretching mode in IR. The intranetwork Mn···Mn separations are 5.941 (via azide) and 11.647 Å (via 4,4′-bipy).

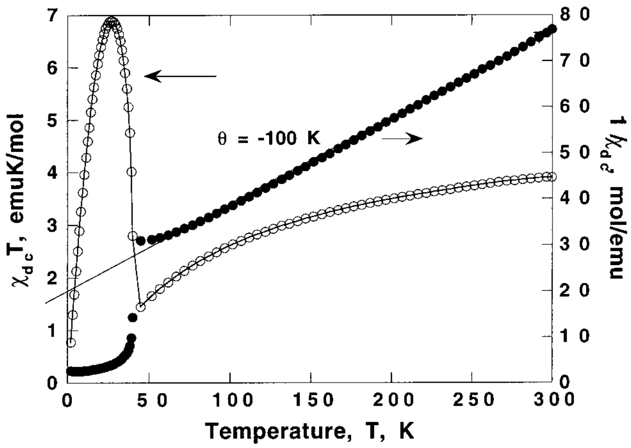

Figure 2. $\chi T(T)$ (○) and reciprocal molar magnetic susceptibility, $1/\chi(T)$ (●), for **1** at 500 Oe.

The 2−300 K magnetic susceptibility, χ, of a polycrystalline sample of **1** could be fit to a Curie−Weiss law above 60 K with $g = 2$ and $\theta = -100$ K, indicating strong nearest-neighbor antiferromagnetic interactions, Figure 2. At 300 K, $\chi T(T)$ has a value of 3.86 emuK/mol and decreases upon cooling due to antiferromagnetic coupling. A sharp increase in $\chi T(T)$ occurs near 45 K whereby a sudden increase is observed, reaching a maximum value of 6.91 emu K/mol at ~30 K. This behavior is characteristic of a spontaneous moment due to spin canting. Below ~30 K, $\chi T(T)$ decreases abruptly down to 2 K owing to increasing antiferromagnetic interactions and/or saturation effects. Moreover, we and others have observed analogous

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(19) Brandon, E. J.; Rittenberg, D. K.; Arif, A. M.; Miller, J. S. *Inorg. Chem.* **1998**, *37*, 3376.

(20) (a) Sheldrick, G. M. *SHELX-86 User Guide*; Crystallographic Department, University of Göttingen: Göttingen, Germany, 1985. (b) Sheldrick, G. M. *SHELX-93 User Guide*; Crystallographic Department, University of Göttingen: Göttingen, Germany, 1993.

(21) Cortés, R.; Urtiaga, M. K.; Lezama, L.; Pizarro, J. L.; Goñi, A.; Arriortua, M. I.; Rojo, T. *Inorg. Chem.* **1994**, *33*, 4009.

Table 1. Summary of the Structure and Magnetic Properties of Representative Extended Azido Structures[a]

compound[a]	bridging mode	magnetic behavior	J, K	T_c, K	ref
Two-Dimensional (2-D)					
$[Mn_2(bpm)(N_3)_4]_n$	EO	ferro−antiferro[d]	*g*	*g*	14
$[Mn(pyz)(N_3)_2]_n$	EO	ferro−antiferro[d]	0.61	<2	15
$[Mn(etinc)_2(N_3)_2]$	EO−EE	ferro−antiferro[b]	*g*	*g*	10
		weak ferro[c]	*g*	16	11
$[Mn(4\text{-}cnpy)_2(N_3)_2]_n$	EO−EE	weak ferro[c]	*g*	18	11
$[Mn(3\text{-}acpy)_2(N_3)_2]_n$	EO−EE	weak ferro[c]	*g*	16	11
$[Mn(minc)_2(N_3)_2]_n$	EO−EE	antiferro[c]	−3.23	*g*	13
$[Mn(4\text{-}acpy)_2(N_3)_2]_n$	EE	antiferro[f]	−5.52	*g*	12
		weak ferro[c]	*g*	28	11
$[Mn(bpe)_2(N_3)_2]_n$	EE	antiferro[f]	−18	*g*	16
Three-Dimensional (3-D)					
$[Mn(py)_2(N_3)_2]_n$	EE	antiferro[b]	−1.94	*g*	10
		weak ferro[c]	*g*	40	11
$[Mn(4,4'\text{-}bipy)_2(N_3)_2]_n$	EE	antiferro[f]	*g*	*g*	17
		weak ferro[e]	*g*	41	*h*
$[N(CH_3)_4][Mn(N_3)_3]_n$	EE	antiferro[f]	−2.5	*g*	18

[a] etinc = ethyl isonicotinate, 4-cnpy = 4-cyanopyridine, 3-acpy = 3-acetylpyridine, 4-acpy = 4-acetylpyridine, minc = methyl isonicotinate, bpm =2,2′-bipyrimidine, pyz = pyrazine, bpe = 1,2-bis(4-pyridyl)ethane, py = pyridine, bipy = bipyridine. [b] 15 kOe. [c] 100 Oe. [d] 1000 Oe. [e] 500 Oe. [f] Magnetic field was not reported. [g] Not reported. [h] This work.

phenomena in the canted antiferromagnet $Mn^{II}[N(CN)_2]_2$.[22] Compound **1** was previously reported as an antiferromagnet.[17] However, for a weak ferromagnet due to spin canting, the magnetic behavior is quite field-dependent. As summarized in Table 1, some Mn−azide compounds showing characteristic antiferromagnetic behavior at higher magnetic field exhibit weak ferromagnetism at lower magnetic field.

Long-range magnetic order is clearly evident from low-field magnetization and ac susceptibility measurements. The divergence of the zero-field (ZFC) and field-cooled (FC) $M(T)$ data below $T_c = 42.5$ K indicates irreversible behavior arising from the formation of a magnetically ordered state. The presence of a nonzero $\chi_{ac}''(T)$ component in the $\chi_{ac}(T)$ data suggests hysteretic effects and an uncompensated moment, Figure 3. $\chi_{ac}'(T)$ exhibits behavior analogous to that of the ZFC/FC data as expected in the low-field dc limit. Small magnetization values at 2 K indicate the presence of a weakly spin canted (noncollinear) moment. The strong magnetic exchange observed for **1** is attributed to the Mn−NNN−Mn interaction as opposed to exchange via the 4,4′-bipy ligand, which would lead to a more 2-D magnetic behavior.

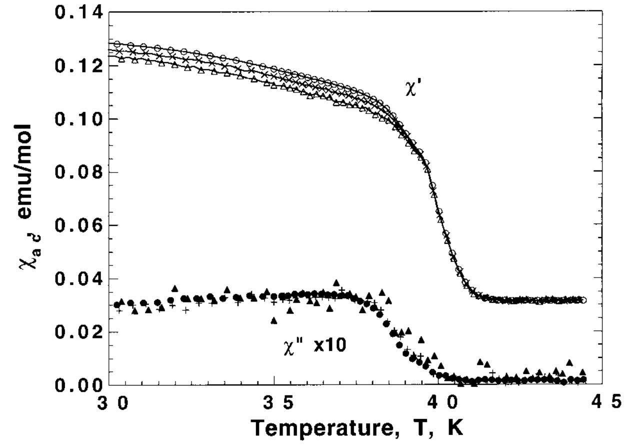

Figure 3. Temperature dependencies of the in-phase (open symbols), χ', and out-of-phase (filled symbols), χ'', ac susceptibility of **1** measured in an oscillating field of 10 (○, ●), 100 (×, +), and 1000 (△, ▲) Hz with an amplitude of 1 Oe.

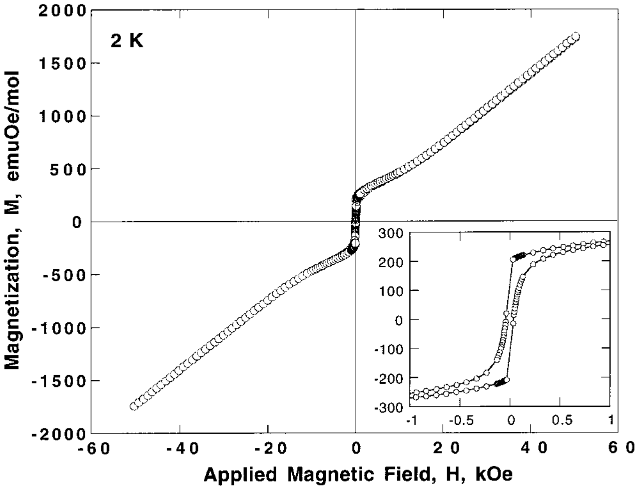

Figure 4. Hysteresis loop of **1** taken at 2 K.

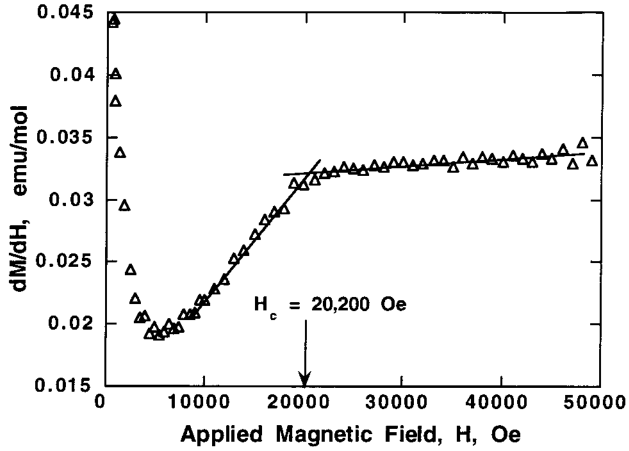

Figure 5. Derivative of the isothermal magnetization with respect to dc field of **1** at 2 K.

The 2 K isothermal magnetization displays an unusual hysteresis curve, Figure 4. Initially, the magnetization rises rapidly to a value of ~200 emu Oe/mol ($H_{dc} < 500$ Oe). Beyond this $M(H)$ rises quasi-linearly to ~1.2 T, whereby an inflection point is observed with an increased slope which is likely attributed to a spin flop transition. Further evidence for a spin reorientation comes from a clear discontinuity in the d$M(H)$/dH data, Figure 5, although single-crystal magnetization measurements are needed to confirm this. At the highest field measured (50 kOe), a low magnetization value of 1750 emu Oe/mol is achieved and saturation does not occur. A coercive field of 40 Oe and remanent magnetization of 200 emu Oe/mol were also observed, Figure 4 (inset). Extrapolating the reversible branch of the hysteresis curve to $H = 0$ gives a saturated moment of 256 emu Oe/mol, and from this, we estimate the spin canting angle, γ, to be ~0.5°.[23] At fields greater than ~1000

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(22) (a) Manson, J. L.; Kmety, C. R.; Epstein, A. J.; Miller, J. S. *Inorg. Chem.* **1999**, *38*, 2552. (b) Kmety, C. R.; Manson, J. L.; Huang, Q.; Lynn, J. W.; Miller, J. S.; Epstein, A. J. Manuscript in preparation. (c) Batten, S. R.; Jensen, P.; Kepert, C. J.; Kurmoo, M.; Moubaraki, B.; Murray, K. S.; Price, D. J. *J. Chem. Soc., Dalton Trans.* **1999**, 2987.

(23) Palacio, F.; Andres, M.; Horne, R.; van Duyneveldt, A. J. *J. Magn. Magn. Mater.* **1986**, *54*, 1487.

Oe the spontaneous moment is destroyed, rendering a typical antiferromagnet, which is likely how Shen et al.[17] acquired their results.

Spin canting may arise provided a mechanism for antisymmetric exchange and/or single-ion anisotropy is present.[24] As this system lacks a center of symmetry and possesses distorted Mn^{II} sites, it is reasonable to expect that the spontaneous moment arises from a Dzyaloshinski–Moriya interaction.[25] However, to better understand the detailed aspects of the magnetic properties of **1**, neutron diffraction experiments are needed. Additionally, we are studying the remainder of the first-row transition metal series of M(4,4′-bipy)$(N_3)_2$ (M = Fe, Co, Ni, Cu).

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(24) (a) Palacio, F. *Mol. Cryst. Liq. Cryst.* **1997**, *305*, 385. (b) Dzyaloshinski, J. *J. Phys. Chem. Solids* **1958**, *4*, 241. (c) Moriya, T. *Phys. Rev.* **1960**, *120*, 91.

(25) (a) Dzyaloshinski, J. *J. Phys. Chem. Solids* **1958**, *4*, 241. (b) Moriya, T. *Phys. Rev.* **1960**, *120*, 91.