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Article

Cyanide-Bridged Mn(III)–Fe(III) Bimetallic Complexes Based on the Pentacyano(1-methylimidazole)ferrate(III) Building Block: Structure and Magnetic Characterizations

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Seven cyanide-bridged bimetallic complexes have been synthesized by the reaction of $[Fe(1\text{-}CH_3im)(CN)_5]^{2-}$ with Mn(III) Schiff base complexes. Their crystal structure and magnetic properties have been characterized. Five complexes, $[Mn_2(5\text{-}Brsalen)_2Fe(CN)_5(1\text{-}CH_3im)]\cdot H_2O$ (**1**), $[Mn_2(5\text{-}Clsalen)_2(H_2O)_2Fe(CN)_5(1\text{-}CH_3im)]\cdot H_2O$ (**2**), $[Mn_2(5\text{-}Clsaltn)_2(H_2O)_2Fe(CN)_5(1\text{-}CH_3im)]$ (**3**), $[Mn_2(5\text{-}Clsaltmen)_2(H_2O)_2Fe(CN)_5(1\text{-}CH_3im)]\cdot H_2O$ (**4**), and $[Mn_2(5\text{-}Brsaltmen)_2(H_2O)_2Fe(CN)_5(1\text{-}CH_3im)]\cdot CH_3OH$ (**5**), are neutral and trinuclear with two $[Mn(SB)]^+$ (SB^{2-} = Schiff base ligands) and one $[Fe(1\text{-}CH_3im)(CN)_5]^{2-}$. Complex $\{[Et_4N][Mn(acacen)Fe(CN)_5(1\text{-}CH_3im)]\}_n\cdot 6nH_2O$ (**6**) is one-dimensional with alternate $[Mn(acacen)]^+$ and $[Fe(CN)_5(1\text{-}CH_3im)]^{2-}$ units. The two-dimensional complex $\{[Mn_4(saltmen)_4Fe(CN)_5(1\text{-}CH_3im)]\}_n[ClO_4]_{2n}\cdot 9nH_2O$ (**7**) consists of Mn₄Fe units which are further connected by the phenoxo oxygen atoms. Magnetic studies show the presence of ferromagnetic Mn(III)–Fe(III) coupling in the trinuclear compounds with the magnetic coupling constant (*J*) ranging from 4.5 to 6.0 cm⁻¹, based on the Hamiltonian $\hat{H} = -2J\hat{S}_{Fe}(\hat{S}_{Mn(1)} + \hat{S}_{Mn(2)})$. Antiferromagnetic interaction has been observed in complex **6**, whereas ferromagnetic coupling occurs in complex **7**. Complexes **6** and **7** exhibit long-range magnetic ordering with a T_N value of 4.0 K for **6** and T_c of 4.8 K for **7**. Complex **6** shows metamagnetic behavior at 2 K, and complex **7** possesses a hysteresis loop with a coercive field of 500 Oe, typical of a soft ferromagnet.

Introduction

During the past decades, more and more attention has been paid to the research of cyanide-bridged complexes because of their remarkable magnetic, magneto-optical, and electrochemical properties.[1−30] Several different approaches have been employed to design molecule-based magnets that exhibit spontaneous magnetization. Many Prussian blue analogues $M_x[M'(CN)_6]_y\cdot nH_2O$ have been synthesized by the reaction

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(1) Sato, O.; Lyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *272*, 704.
(2) Mallah, T.; Thiebaut, S.; Verdaguer, M.; Veillet, P. *Science* **1993**, *262*, 1554.
(3) (a) Holmes, S. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1999**, *121*, 5593. (b) Hatlevik, O.; Buschmann, W. E.; Manson, J. L. *Adv. Mater.* **1999**, *11*, 914. (c) Bleuzen, A.; Lomenech, C.; Escax, V.; Villain, F.; Varret, F.; Cartier dit Moulin, C.; Verdaguer, M. *J. Am. Chem. Soc.* **2000**, *122*, 6648.
(4) Ohba, M.; Maruono, N.; Okawa, H.; Enoki, T.; Lator, J.-M. *J. Am. Chem. Soc.* **1994**, *116*, 11566.
(5) Ohba, M.; Okawa, H. *Coord. Chem. Rev.* **2000**, *198*, 313.
(6) Baraldo, L. M.; Forlano, P.; Parise, A. R.; Slep, L. D.; Olabe, J. A. *Coord. Chem. Rev.* **2001**, *219−221*, 881.
(7) Alcock, N. W.; Samotus, A.; Szklarzewicz, J. *J. Chem. Soc., Dalton Trans.* **1993**, *885*.
(8) El Fallah, M. S.; Rentschler, E.; Caneschi, A.; Sessoli, R.; Gatteschi, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1947.
(9) Yi, X.-Y.; Liu, B.; Jiménez-Aparicio, R.; Urbanos, F. A.; Gao, S.; Xu, W.; Chen, J. S.; Song, Y.; Zheng, L.-M. *Inorg. Chem.* **2005**, *44*, 4309.
(10) Gheorghe, R.; Andruh, M.; Costes, J.-P.; Donnadieu, B. *Chem. Commun.* **2003**, 2778.
(11) Kou, H.-Z.; Zhou, B. C.; Si, S.-F.; Wang, R.-J. *Eur. J. Inorg. Chem.* **2004**, 401.
(12) Marvaud, V.; Decroix, C.; Scuiller, A.; Guyard-Duhayon, C.; Vaissermann, J.; Gonnet, F.; Verdaguer, M. *Chem.—Eur. J.* **2003**, *9*, 1678.
(13) Van Langenberg, K.; Batten, S. R.; Berry, K. J.; Hockless, D. C. R.; Moubaraki, B.; Murray, K. S. *Inorg. Chem.* **1997**, *36*, 5006.
(14) Karadas, F.; Schelter, E. J.; Prosvirin, A. V.; Bacsa, J.; Dunbar, K. R. *Chem. Commun.* **2005**, 1414.
(15) Vostrikova, K. E.; Luneau, D.; Wernsdorfer, W.; Rey, P.; Verdaguer, M. *J. Am. Chem. Soc.* **2000**, *122*, 718.
(16) Zhong, Z. J.; Seino, H.; Mizobe, Y.; Hidai, M.; Fujishima, A.; Ohkoshi, S.; Hashimoto, K. *J. Am. Chem. Soc.* **2000**, *122*, 2952.
(17) Larionova, J.; Gross, M.; Pilkington, M.; Andres, H.; Stoeckli-Evans, H.; Gdel, H. U.; Decurtins, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1605.
(18) Parker, R. J.; Spiccia, L.; Berry, K. J.; Fallon, G. D.; Moubaraki, B.; Murray, K. S. *Chem. Commun.* **2001**, 333.
(19) Colacio, E.; Domínguez-Vera, J. M.; Lloret, F.; Rodríguez, A.; Stoeckli-Evans, H. *Inorg. Chem.* **2003**, *42*, 6962.
(20) Ohba, M.; Usuki, N.; Fukita, N.; Okawa, H. *Inorg. Chem.* **1998**, *37*, 3349.

of cyanide-containing building blocks $[M'(CN)_6]^{3-}$ ($M' =$ Fe, Cr, Mn) with other paramagnetic metallic complexes $[M(H_2O)_6]^{m+}$, and some of them exhibit long-range magnetic ordering at considerably high temperatures.[3]

Hybrid Prussian blue complexes were later introduced[4] using the coordinatively unsaturated complexes $[M(L)]^{m+}$ (where L represents polydentate ligands) instead of $[M(H_2O)_6]^{m+}$ to react with $[M'(CN)_6]^{3-}$. By the alteration of the organic ligands L, a series of polynuclear,[12−18] 1D,[19−21] 2D,[22−24] and 3D[25−28] complexes have been synthesized, which exhibit ferro-, antiferro-, ferri-, or metamagnetic behavior. This approach favors better crystallization and therefore magneto-structural studies, and it affords a rich family of structurally and magnetically different complexes.

Another strategy involving the inclusion of a ligand L to cyanide-containing building blocks, $[M(L)(CN)_x]^{n-}$ ($x = 1-5$) instead of $[M'(CN)_6]^{3-}$, has been developed.[31−44] The presence of L usually lowers the dimensionality of the species and, in the meantime, results in novel molecular structures. It should be noted that some complexes exhibiting SMM (single-molecule magnet)[38e,39,40,41a] or SCM (single-chain magnet)[41b,42a,42b] behavior have been obtained using this approach.

However, among these CN^--containing precursors, $[M(L)-(CN)_5]^{n-}$ (L is a monodentate ligand) has been seldom studied.[44] Interested in the building block $[Fe(1-CH_3im)-(CN)_5]^{2-}$ (1-CH_3im stands for 1-methylimidazole),[45] we noticed that $[Fe(1-CH_3im)(CN)_5]^{2-}$ has two interesting characteristics that are different from $[Fe(CN)_6]^{3-}$: (i) the electronic configuration $[3d^5, (3d_{xz})^2(3d_{yz})^2(3d_{xy})^1]$ of the low-spin Fe(III) ion together with the approximate C_{4v} symmetry of $[Fe(1-CH_3im)(CN)_5]^{2-}$ and (ii) the divalent form of the anion which should give rise to complexes structurally different from that derived from $[Fe(CN)_6]^{3-}$. We used it in our first attempt to perform a reaction with $[Mn^{III}(SB)]^+$ complexes (SB stands for Schiff base ligands), for the interest of the versatile and flexible structures of $[Mn(SB)]^+$ complexes that have been widely used to synthesize SMM or SCM complexes.[29,30,46−50] Herein, we report the synthesis,

(21) El Fallah, M. S.; Ribas, J.; Solans, X.; Font-Bardia, M. *New J. Chem.* **2003**, *27*, 895.

(22) Coronado, E.; Gómez-García, C. J.; Nuez, A.; Romero, F. M.; Rusanov, E.; Stoeckli-Evans, H. *Inorg. Chem.* **2002**, *41*, 4615.

(23) Smith, J. A.; Galán-Mascarós, J.-R.; Clérac, R.; Dunbar, K. R. *Chem. Commun.* **2000**, 1077.

(24) Thétiot, F.; Triki, S.; Pala, J. S.; Gómez-García, C. J.; Golhen, S. *Chem. Commun.* **2002**, 1078.

(25) Kou, H.-Z.; Gao, S.; Zhang, J.; Wen, G.-H.; Su, G.; Zheng, R. K.; Zhang, X. X. *J. Am. Chem. Soc.* **2001**, *123*, 11809.

(26) Entley, W. R.; Girolami, G. S. *Inorg. Chem.* **1994**, *33*, 5165.

(27) Zhang, S. W.; Fu, D. G.; Sun, W. Y.; Hu, Z.; Yu, K. B.; Tang, W. X. *Inorg. Chem.* **2000**, *39*, 1142.

(28) Dong, W.; Zhu, L.-N.; Song, H.-B.; Liao, D.-Z.; Jiang, Z.-H.; Yan, S.-P.; Cheng, P. *Inorg. Chem.* **2004**, *43*, 2465.

(29) (a) Miyasaka, H.; Matsumoto, N.; Okawa, H.; Re, N.; Gallo, E.; Floriani, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1446. (b) Miyasaka, H.; Matsumoto, N.; Okawa, H.; Re, N.; Gallo, E.; Floriani, C. *J. Am. Chem. Soc.* **1996**, *118*, 981. (c) Miyasaka, H.; Ieda, H.; Matsumoto, N.; Re, N.; Crescenzi, R.; Floriani, C. *Inorg. Chem.* **1998**, *37*, 255. (d) Miyasaka, H.; Matsumoto, N.; Re, N.; Gallo, E.; Floriani, C. *Inorg. Chem.* **1997**, *36*, 670. (e) Ferbinteanu, M.; Miyasaka, H.; Wernsdorfer, W.; Nakata, K.; Sugiura, K.; Yamashita, M.; Coulon, C.; Clérac, R. *J. Am. Chem. Soc.* **2005**, *127*, 3090. (f) Miyasaka, H.; Takahashi, H.; Madanbashi, T.; Sugiura, K.; Clérac, R.; Nojiri, H. *Inorg. Chem.* **2005**, *44*, 5969. (g) Miyasaka, H.; Ieda, H.; Matsumoto, N.; Sugiura, K.; Yamashita, M. *Inorg. Chem.* **2003**, *42*, 3509. (h) Miyasaka, H.; Okawa, H.; Miyazaki, A.; Enoki, T. *J. Chem. Soc., Dalton Trans.* **1998**, 3991.

(30) (a) Re, N.; Gallo, E.; Floriani, C.; Miyasaka, H.; Matsumoto, N. *Inorg. Chem.* **1996**, *35*, 6004. (b) Miyasaka, H.; Okawa, H.; Miyazaki, A.; Enoki, T. *Inorg. Chem.* **1998**, *37*, 4878.

(31) Abbati, G. L.; Caneschi, A.; Cornia, A.; Fabretti, A. C.; Pozdniakova, Y. A.; Shchegolikhina, O. I. *Angew. Chem., Int. Ed.* **2002**, *41*, 4517.

(32) Oshio, H.; Tamada, O.; Onodera, H.; Ito, T.; Ikoma, T.; Tero-Kubota, S. *Inorg. Chem.* **1999**, *38*, 5686.

(33) Hayami, S.; Gu, Z.-Z.; Einaga, Y.; Kobayasi, Y.; Ishikawa, Y.; Yamada, Y.; Fujishima, A.; Sato, O. *Inorg. Chem.* **2001**, *40*, 3240.

(34) (a) Ni, Z.-H.; Kou, H.-Z.; Zhang, L.-F.; Ge, C.; Cui, A.-L.; Wang, R.-J.; Li, Y.; Sato, O. *Angew. Chem., Int. Ed.* **2005**, *44*, 7742. (b) Ni, Z.-H.; Kou, H.-Z.; Zhang, L.-F.; Zheng, L.; Wang, R.-J.; Cui, A.-L.; Sato, O. *Inorg. Chem.* **2005**, *44*, 2050.

(35) Matsumoto, N.; Sunatsuki, Y.; Miyasaka, H.; Hashimoto, Y.; Luneau, D.; Tuchagues, J.-P. *Angew. Chem., Int. Ed.* **1999**, *38*, 171.

(36) (a) Yeung, W.-F.; Man, W.-L.; Wong, W.-T.; Lau, T.-C.; Gao, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 3031. (b) Yeung, W.-F.; Lau, P.-H.; Lau, T.-C.; Wei, H.-Y.; Sun, H.-L.; Gao, S.; Chen, Z.-D.; Wong, W.-T. *Inorg. Chem.* **2005**, *44*, 6579.

(37) (a) Lescouëzëc, R.; Vaissermann, J.; Lloret, F.; Julve, M.; Verdaguer, M. *Inorg. Chem.* **2002**, *41*, 5943. (b) Lescouëzëc, R.; Vaissermann, J.; Toma, L. M.; Carrasco, R.; Lloret, F.; Julve, M. *Inorg. Chem.* **2004**, *43*, 2234.

(38) (a) Yang, J. Y.; Shores, M. P.; Sokol, J. J.; Long, J. R. *Inorg. Chem.* **2003**, *42*, 1403. (b) Berseth, P. A.; Sokol, J. J.; Shores, M. P.; Heinrich, J. L.; Long, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 9655. (c) Sokol, J. J.; Shores, M. P.; Long, J. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 236. (d) Shores, M. P.; Sokol, J. J.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 2279. (e) Sokol, J. J.; Hee, A. G.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 7656.

(39) Li, D.; Parkin, S.; Wang, G.; Yee, G. T.; Prosvirin, A. V.; Holmes, S. M. *Inorg. Chem.* **2005**, *44*, 4903.

(40) Schelter, E. J.; Prosvirin, A. V.; Dunbar, K. R. *J. Am. Chem. Soc.* **2004**, *126*, 15004.

(41) (a) Wang, S.; Zuo, J.-L.; Zhou, H.-C.; Choi, H. J.; Ke, Y.; Long, J. R.; You, X.-Z. *Angew. Chem., Int. Ed.* **2004**, *43*, 5940. (b) Wang, S.; Zuo, J.-L.; Gao, S.; Song, Y.; Zhou, H.-C.; Zhang, Y.-Z.; You, X.-Z. *J. Am. Chem. Soc.* **2004**, *126*, 8900.

(42) (a) Lescouëzec, R.; Vaissermann, J.; Ruiz-Pérez, C.; Lloret, F.; Carrasco, R.; Julve, M.; Verdaguer, M.; Dromzee, Y.; Gatteschi, D.; Wernsdorfer, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 1483. (b) Toma, L. M.; Lescouëzec, R.; Lloret, F.; Julve, M.; Vaissermann, J.; Verdaguer, M. *Chem. Commun.* **2003**, 1850. (c) Lescouëzec, R.; Lloret, F.; Julve, M.; Vaissermann, J.; Verdaguer, M.; Llusar, R.; Uriel, S. *Inorg. Chem.* **2001**, *40*, 2065. (d) Lescouëzec, R.; Lloret, F.; Julve, M.; Vaissermann, J.; Verdaguer, M. *Inorg. Chem.* **2002**, *41*, 818. (e) Toma, L. M.; Lescouëzec, R.; Toma, L. D.; Lloret, F.; Julve, M.; Vaissermann, J.; Andruh, M. *J. Chem. Soc., Dalton Trans.* **2002**, 3171.

(43) (a) Zhang, Y.-Z.; Gao, S.; Wang, Z.-M.; Su, G.; Sun, H.-L.; Pan, F. *Inorg. Chem.* **2005**, *44*, 4534. (b) Zhang, Y.-Z.; Gao, S.; Sun, H.-L.; Su, G.; Wang, Z.-M.; Zhang, S.-W. *Chem. Commun.* **2004**, 1906.

(44) Culp, J. T.; Park, J. H.; Meisel, M. W.; Talham, D. R. *Inorg. Chem.* **2003**, *42*, 2842.

(45) (a) Johnson, C. R.; Shepherd, R. E. *Synth. React. Inorg. Met.−Org. Chem.*, **1984**, *14*, 339. (b) Johnson, C. R.; Shepherd, R. E.; Marr, B.; O'Donnell, S.; Dressick, W. *J. Am. Chem. Soc.* **1980**, *102*, 6227. (c) Johnson, C. R.; Shepherd, R. E. *Inorg. Chem.* **1983**, *22*, 3506. (d) Johnson, C. R.; Jones, C. M.; Asher, S. A.; Abola, J. E. *Inorg. Chem.* **1991**, *30*, 2120.

(46) (a) Przychodzeń, P.; Lewiński, K.; Bałanda, M.; Pełka, R.; Rams, M.; Wasiutyński, T.; Guyard-Duhayon, C.; Sieklucka, B. *Inorg. Chem.* **2004**, *43*, 2967. (b) Przychodzeń, P.; Rams, M.; Guyard-Duhayon, C.; Sieklucka, B. *Inorg. Chem. Commun.* **2005**, *8*, 350.

(47) Kou, H.-Z.; Ni, Z.-H.; Zhou, B.-C.; Wang, R.-J. *Inorg. Chem. Commun.* **2004**, *7*, 1150.

(48) (a) Choi, H. J.; Sokol, J. J.; Long, J. R. *J. Phys. Chem. Solids.* **2004**, *65*, 839. (b) Shen, X.; Li, B.; Zou, J.; Xu, Z. *Transition Met. Chem.* **2002**, *27*, 372. (c) Choi, H. J.; Sokol, J. J.; Long, J. R. *Inorg. Chem.* **2004**, *43*, 1606.

(49) (a) Miyasaka, H.; Nezu, T.; Sugimoto, K.; Sugiura, K.; Yamashita, M.; Clérac, R. *Inorg. Chem.* **2004**, *43*, 5486. (b) Miyasaka, H.; Clérac, R.; Mizushima, K.; Sugiura, K.; Yamashita, M.; Wernsdorfer, W.; Coulon, C. *Inorg. Chem.* **2003**, *42*, 8203. (c) Miyasaka, H.; Nezu, T.; Sugimoto, K.; Sugiura, K.; Yamashita, M.; Clérac, R. *Chem.−Eur. J.* **2005**, *11*, 1592.

(50) Si, S.-F.; Tang, J.-K.; Liu, Z.-Q.; Liao, D.-Z.; Jiang, Z.-H.; Yan, S.-P.; Cheng, P. *Inorg. Chem. Commun.* **2003**, *6*, 1109.

Scheme 1. Schematic Illustration of the [Mn(SB)]$^+$ Compounds
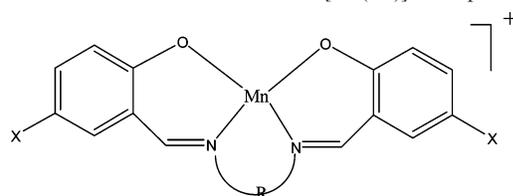
SB	R	X
5-Brsalen^{2-}	CH_2CH_2	Br
5-Clsalen^{2-}	CH_2CH_2	Cl
5-Clsaltn^{2-}	$CH_2CH_2CH_2$	Cl
saltmen^{2-}	$C(CH_3)_2C(CH_3)_2$	H
5-Clsaltmen^{2-}	$C(CH_3)_2C(CH_3)_2$	Cl
5-Brsaltmen^{2-}	$C(CH_3)_2C(CH_3)_2$	Br
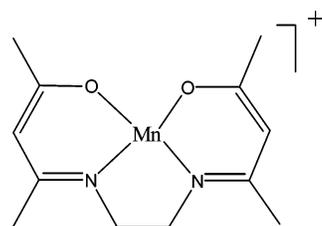
SB = acacen^{2-}

crystal structures, and magnetic properties of seven complexes derived from [Mn(SB)]$^+$ and [Fe(1-CH$_3$im)(CN)$_5$]$^{2-}$. The [Mn(SB)]$^+$ complexes employed in the experiments are shown in Scheme 1.

Experimental Section

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementary Vario El. The infrared spectroscopy on KBr pellets was performed on a Magna-IR 750 spectrophotometer in the 4000−400 cm^{-1} region. Magnetic measurements were performed on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).[51]

Synthesis. All chemicals and solvents used for the synthesis were reagent grade. The precursor, [Mg(1-CH$_3$im)$_2$(H$_2$O)$_2$Fe(CN)$_5$(1-CH$_3$im)]·H$_2$O, was prepared according to the literature method.[45d] The Mn(III) Schiff base compounds [Mn(5-Brsalen)(H$_2$O)]ClO$_4$, [Mn(5-Clsalen)(H$_2$O)]ClO$_4$, [Mn(5-Clsaltn)(H$_2$O)]ClO$_4$, [Mn(saltmen)-(H$_2$O)]ClO$_4$, [Mn(5-Brsaltmen)(H$_2$O)]ClO$_4$, [Mn(5-Clsaltmen)-(H$_2$O)]ClO$_4$, and [Mn(acacen)]ClO$_4$ were prepared as described elsewhere.[29,46,47] ***Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled in small quantities with care.***

Complexes 1−5 and 7. The compounds were similarly prepared as dark brown crystals with the use of appropriate manganese(III) Schiff base complexes; therefore, only the synthesis of complex **1** was described in detail. A methanol solution (10 mL) of [Mn(5-Brsalen)(H$_2$O)]ClO$_4$ (0.2 mmol, 101.6 mg) was carefully layered onto an aqueous solution (10 mL) of [Mg(1-CH$_3$im)$_2$(H$_2$O)$_2$Fe(CN)$_5$-(1-CH$_3$im)]·H$_2$O (0.1 mmol, 51.1 mg). After the mixture stood for a few weeks in a dark room, dark brown crystals suitable for X-ray diffraction were obtained. They were filtered, washed with 1:1 (v/v) methanol−water, and dried at room temperature. Complex **1**. Yield: 43.2 mg (33.7%). Anal. Calcd. for FeMn$_2$C$_{41}$N$_{11}$H$_{36}$O$_7$Br$_4$:

C, 38.47; H, 2.83; N, 12.04. Found: C, 38.70; H, 3.06; N, 12.25. IR (KBr): ν 2137, 2110 (C≡N), 1633 cm^{-1} (C=N). Complex **2**. Yield: 47.4 mg (43.0%). Anal. Calcd. for FeMn$_2$C$_{41}$N$_{11}$H$_{36}$O$_7$Cl$_4$: C, 44.67; H, 3.29; N, 13.98. Found: C, 44.84; H, 3.36; N, 13.99. IR (KBr): ν 2119 (C≡N), 1631 cm^{-1} (C=N). Complex **3**. Yield: 25.6 mg (23%). Anal. Calcd for FeMn$_2$C$_{43}$N$_{11}$H$_{38}$O$_6$Cl$_4$: C, 45.69; H, 3.57; N, 13.85. Found: C, 45.83; H, 3.44; N, 13.52. IR (KBr): ν 2127 (C≡N), 1617 cm^{-1} (C=N). Complex **4**. Yield: 45.6 mg (37.5%). Anal. Calcd for FeMn$_2$C$_{49}$N$_{11}$H$_{52}$O$_7$Cl$_4$: C, 48.46; H, 4.32; N, 12.69. Found: C, 48.07; H, 4.37; N, 13.11. IR (KBr): ν 2130, 2117 (C≡N), 1608 cm^{-1} (C=N). Complex **5**. Yield: 25 mg (17.8%). Anal. Calcd for FeMn$_2$C$_{50}$H$_{54}$N$_{11}$O$_7$Br$_4$: C, 42.80; H, 3.88; N, 10.99. Found: C, 43.01; H, 4.07; N, 10.81. IR (KBr): ν 2129, 2115 (C≡N), 1613 cm^{-1} (C=N). Complex **7**. Yield: 30.4 mg (28.4%). Anal. Calcd for FeMn$_4$C$_{89}$N$_{15}$H$_{112}$O$_{25}$Cl$_2$: C, 49.99; H, 5.28; N, 9.82. Found: C, 50.01; H, 5.17; N, 10.18. IR (KBr): ν 2125 (C≡N), 1602 (C=N), 1097 cm^{-1} (Cl−O).

{[Et$_4$N][Mn(acacen)Fe(CN)$_5$(1-CH$_3$im)]}$_n$·6nH$_2$O (6). Complex **6** was synthesized by a similar procedure for the synthesis of [Et$_4$N]$_2$[Mn(acacen)Fe(CN)$_6$].[30a] To an ethanol solution (20 mL) of Et$_4$NBr (0.2 mmol, 42.0 mg) was added [Mg(1-CH$_3$im)$_2$(H$_2$O)$_2$-Fe(CN)$_5$(1-CH$_3$im)]·H$_2$O (0.1 mmol, 51.0 mg). A minimum amount of water (1 mL) was added to this mixture, and it was stirred at room temperature until the solids dissolved completely. The resulting solution was then added dropwise to an ethanol solution (10 mL) of [Mn(acacen)]ClO$_4$ (0.1 mmol, 37.7 mg). After filtration, the filtrate was added to 20 mL of 2-propanol, and then the mixture was allowed to stand in the dark. After a few days, dark brown platelet single crystals suitable for X-ray diffraction formed. They were collected by filtration, washed with 1:1 (v/v) 2-propanol−ethanol, and dried at room temperature. Yield: 23.5 mg (30%). Anal. Calcd. for FeMnC$_{29}$N$_{10}$H$_{56}$O$_8$: C, 44.45; H, 7.20; N, 17.87. Found: C, 44.30; H, 6.96; N, 18.09. IR (KBr): ν 2115 (C≡N), 1593 cm^{-1} (C=N).

X-ray Structure Determinations. The data collections of **1** and **2−7** were made on a computer-controlled Siemens P4 diffractometer and a Rigaku R-axis rapid IP equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), respectively. All the structures were solved by the direct method (SHELXS-97) and refined by full matrix least-squares (SHELXL-97) on F^2. Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined by using a riding model. In complex **2**, the 1-methylimidazole and its opposite cyano groups around the Fe(III) ion experience disorder. In complex **6**, disorder also exists in the tetraethylammonium cations over two symmetry-related sets of positions. In complex **7**, when the compound crystallized in the space group *I*4/*m*, the presence of a C_4 rotational axis through the Fe(1) [0.500, 0.500, 0.227], C(2) [0.500, 0.500, 0.156], and N(2) [0.500, 0.500, 0.114] atoms results in the disorder of the 1-methylimidazole group opposite to the cyano ligand C(2)−N(2). The interlayer perchlorate ions and water molecules could not be accurately determined. We have tried different single crystals of complex **7** for X-ray diffraction, but the R factors could not be lowered markedly. Nevertheless, the positions of the intralayer atoms were satisfactorily determined.

Results and Discussion

Synthesis and General Characterization. Because the coordination bonds between Mg^{2+} and the cyanides are weak, [Mg(1-CH$_3$im)$_2$(H$_2$O)$_2$Fe(CN)$_5$(1-CH$_3$im)]·H$_2$O is soluble in water to generate free [Fe(CN)$_5$(1-CH$_3$im)]$^{2-}$ anions, which

(51) (a) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986. (b) Kahn, O. *Molecular Magnetism*; Wiley-VCH: New York, 1993.

Table 1. Crystallographic Data for Complexes **1**−**7**

	1	**2**	**3**	**4**
formula	FeMn$_2$C$_{41}$H$_{36}$N$_{11}$O$_7$Br$_4$	FeMn$_2$C$_{41}$H$_{36}$N$_{11}$O$_7$Cl$_4$	FeMn$_2$C$_{48}$H$_{36}$N$_{11}$O$_6$Cl$_4$	FeMn$_2$C$_{49}$H$_{52}$N$_{11}$O$_7$Cl$_4$
fw	1280.18	1102.34	1112.37	1214.55
T (K)	296	123	113	293
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$Pca2_1$	$P2_1/c$
a (Å)	13.4412(6)	11.265(3)	15.011(3)	14.892(3)
b (Å)	18.8460(8)	13.885(4)	28.739(6)	14.443(3)
c (Å)	19.6663(8)	15.027(4)	21.756(4)	25.420(5)
β (deg)	102.2640(10)	92.0390(10)		93.00(3)
V (Å^3)	4868.0(4)	2349.0(12)	9386(3)	5460.0(19)
Z	4	2	8	4
ρ_{calcd} (g cm^{-3})	1.747	1.559	1.574	1.478
F(000)	2524	1118	4520	2492
data/restraints/params	9579/0/604	4569/0/332	18329/1/1208	9271/0/668
R1 [$I > 2\sigma(I)$]	0.0585	0.0725	0.0653	0.0570
wR2 (all data)	0.1362	0.1604	0.1195	0.0926

	5	**6**	**7**
formula	FeMn$_2$C$_{50}$H$_{54}$N$_{11}$O$_7$Br$_4$	FeMnC$_{29}$H$_{56}$N$_{10}$O$_8$	FeMn$_4$C$_{89}$H$_{112}$N$_{15}$O$_{25}$Cl$_2$
fw	1406.41	783.63	2138.45
T (K)	293	123	173
cryst syst	monoclinic	orthorhombic	tetragonal
space group	$P2_1/c$	$Pbcm$	$I4/m$
a (Å)	14.966(7)	11.994(3)	18.805(3)
b (Å)	14.423(7)	18.333(4)	18.805(3)
c (Å)	25.709(10)	17.220(4)	27.473(6)
β (deg)	92.97(2)		
V (Å^3)	5542(4)	3786.6(14)	9715(3)
Z	4	4	4
ρ_{calcd} (g cm^{-3})	1.686	1.375	1.462
F (000)	2812	1660	4444
data/restraints/params	19635/0/677	3233/0/299	4887/0/332
R1 [$I > 2\sigma(I)$]	0.0497	0.0735	0.1326
wR2 (all data)	0.1344	0.1619	0.2885

makes it possible to prepare new cyanide-bridged magnetic materials. Complexes **1**−**5** and **7** were all obtained as well-shaped single crystals by the reactions of the appropriate [Mn(SB)(H$_2$O)]ClO$_4$ complexes with [Mg(1-CH$_3$im)$_2$(H$_2$O)$_2$-Fe(CN)$_5$(1-CH$_3$im)]·H$_2$O in a molar ratio of 2:1 by the slow diffusion method, while complex **6** was synthesized in the presence of a large countercation [Et$_4$N]$^+$. Because of the divalent form of the [Fe(CN)$_5$(1-CH$_3$im)]$^{2-}$ building block and the 2:1 molar ratio of Mn:Fe in the final products, the trinuclear products are neutral. The introduction of different [Mn(SB)]$^+$ compounds results in structurally different products: cis-trinuclear for **1**, trans-trinuclear for **2**−**5**, 1D chain for **6**, and 2D network for **7**.

Infrared spectra for complexes **1**−**7** show one or two peaks in the range of 2110−2130 cm^{-1}, which are attributable to the C≡N stretching vibration of cyano ligands. The IR spectrum of complex **7** exhibits a strong absorption at 1097 cm^{-1}, which can be assigned to the Cl−O stretching vibration for the perchlorate anions. This is consistent with the presence of ClO$_4^-$ anions from the single-crystal X-ray data.

Detailed crystallographic data for all compounds are listed in Table 1. The labeling schemes for the crystal structures of complexes **1**−**7** are depicted in Figures 1−5 and in the Supporting Information, and selected bond length and angles are presented in Tables 2−5. The relevant bond distances and angles for **3** and **7** are given as Supporting Information.

Crystal Structures. The asymmetric unit of complex **1** consists of one [Fe(CN)$_5$(1-CH$_3$im)]$^{2-}$ anion and two [Mn(5-Brsalen)]$^+$ cations, as shown in Figure 1. Each [Fe(CN)$_5$(1-CH$_3$im)]$^{2-}$ unit uses two *cis*-cyano groups to connect with two [Mn(5-Brsalen)]$^+$ groups, whereas the three remaining CN$^-$ units are terminal. Two cis-bridging cyanides are in the equatorial plane of Fe(III) coordination octahedron. The C−Fe−C bond angles are very close to 90°, while the N(6)−Fe(1)−C(4) group is nearly linear. The Fe−C distances range from 1.924(8)−1.938(7) Å, whereas the Fe−N distance of 1.988(5) Å is a little longer than that of 1.950(2) Å in the precursor [Mg(1-CH$_3$im)(H$_2$O)$_2$Fe(CN)$_5$(1-CH$_3$im)]·H$_2$O.[45d]

The coordination geometry of the Mn(III) ion in complex **1** is elongated octahedral because of the Jahn−Teller Effect of the high-spin d^4 electronic configuration of Mn(III). The equatorial sites are occupied by the N$_2$O$_2$ donor atoms of the 5-Brsalen^{2-} ligand with average bond distances of Mn−N = 1.976(5) Å and Mn−O = 1.880(4) Å, while the two axial positions are occupied by the N atom of the cyanide group of [Fe(CN)$_5$(1-CH$_3$im)]$^{2-}$ and a water molecule with the Mn−O distances of 2.289(4) Å for Mn(1)−O(1W) and 2.266(4) Å for Mn(1)−O(2W). The Mn(1)−N(1) and Mn(2)−N(2) bond distances are 2.236(6) and 2.222(6) Å, respectively, and the Mn−N≡C bond angles are bent [Mn(1)−N(1)−C(1) = 160.0(5)° and Mn(2)−N(4)−C(4) = 154.3(5)°]. The adjacent Fe−Mn distances are 5.250(5) Å for Fe(1)−Mn(1) and 5.119(5) Å for Fe(1)−Mn(2). The bond distances and angles are similar to those found in the [Mn(SB)]$_m$[Fe(CN)$_6$]$_n$ complexes.[29c,29d]

Figure 1b shows the cell packing diagram of complex **1** along the a axis. There are hydrogen-bond interactions among the cyano nitrogen atoms (N(3) and N(5)) of the trinuclear

Table 3. Selected Bond Distances (Å) and Angles (deg) of Complex **2**

Fe(1)−C(1)	1.918(6)	Fe(1)−C(2)	1.939(5)
Fe(1)−C(3)	1.86(3)	Fe(1)−N(4)	2.039(7)
Mn(1)−N(1)	2.243(5)	Mn(1)−O(1W)	2.231(3)
Mn(1)−O(1)	1.879(4)	Mn(1)−O(2)	1.883(4)
Mn(1)−N(6)	1.994(5)	Mn(1)−N(7)	1.993(5)
Mn(1)−N(1)−C(1)	149.8(5)	N(1)−C(1)−Fe(1)	177.9(5)
N(2)−C(2)−Fe(1)	179.7(6)	N(3)−C(3)−Fe(1)	167(3)

Table 4. Selected Bond Distances (Å) and Angles (deg) of Complexes **4** and **5**

	4	**5**
Fe(1)−C(1)	1.941(3)	1.948(3)
Fe(1)−C(2)	1.928(3)	1.935(3)
Fe(1)−C(3)	1.917(4)	1.926(3)
Fe(1)−C(4)	1.950(4)	1.942(3)
Fe(1)−C(5)	1.941(4)	1.943(3)
Fe(1)−N(6)	2.008(3)	2.009(3)
Mn(1)−N(1)	2.311(3)	2.323(3)
Mn(2)−N(2)	2.258(3)	2.266(3)
Mn(1)−O(1W)	2.323(3)	2.333(3)
Mn(1)−O(1)	1.878(3)	1.885(2)
Mn(1)−O(2)	1.858(3)	1.882(2)
Mn(1)−N(8)	1.987(3)	1.991(2)
Mn(1)−N(9)	2.000(3)	1.986(2)
Mn(2)−O(3)	1.894(3)	1.893(2)
Mn(2)−O(4)	1.862(3)	1.876(2)
Mn(2)−N(10)	1.984(3)	1.981(3)
Mn(2)−N(11)	1.984(3)	1.986(3)
Mn(2)−O(2W)	2.422(2)	2.429(3)
Mn(1)−N(1)−C(1)	159.7(3)	159.4(2)
Mn(2)−N(2)−C(2)	157.8(3)	157.2(3)
N(1)−C(1)−Fe(1)	176.5(3)	177.4(3)
N(2)−C(2)−Fe(1)	175.1(3)	175.0(3)

Table 5. Selected Bond Distances (Å) and Angles (deg) of Complex **6**

Fe(1)−C(7)	1.949(5)	Fe(1)−C(8)	1.943(8)
Fe(1)−C(9)	1.946(5)	Fe(1)−N(5)	1.979(6)
Mn(1)−N(1)	1.979(4)	Mn(1)−N(2)	2.331(4)
Mn(1)−O(1)	1.902(3)		
Fe(1)−C(7)−N(2)	177.7(4)	C(7)−N(2)−Mn(1)	144.4(4)

Complexes **2**−**5** are all trans-trinuclear and are similar to each other. In complex **2**, the 1-methylimidazole and its opposite CN⁻ groups are disordered (see Figure 2); for complex **3**, each unit cell consists of two independent trans-trinuclear units, one of which is shown in Figure S1. Figure 3 shows the structure of complex **4** to which the structures of complexes **3**−**5** are similar.

In all the trans-trinuclear compounds, **2**−**5**, the [Fe(CN)₅-(1-CH₃im)]²⁻ unit uses two *trans*-CN⁻ groups in the equatorial plane to connect two [Mn(SB)]⁺ groups. The axial CN⁻ group opposite to the 1-methylimidazole ligand is monodentate. All Fe−C distances range from 1.917(4) to 1.969(6) Å (excluding the disordered CN⁻ in complex **2**, Fe(1)−C(3) = 1.86(3) Å), and all the Fe−C≡N linkages are always linear. The Fe−N$_{\text{imidazole}}$ distances in all complexes have similar values, ranging from 1.990(5) to 2.039(7) Å. The Mn(III) ions are coordinated equatorially by N₂O₂ donors of the tetradentate Schiff base ligands and axially by a cyano nitrogen atom of [Fe(CN)₅(1-CH₃im)]²⁻ with Mn−N$_{\text{cyano}}$ bond distances ranging from 2.221(5) to 2.323(3) Å and a water oxygen atom (Mn−O$_{\text{water}}$ bond distance range of 2.222(4)−2.429(3) Å), giving rise to an elongated octahedral coordination geometry. The bridging cyano ligands coordi-

Figure 1. (a) cis-Trinuclear structure of complex **1** with atom-labeling scheme showing 30% probability thermal ellipsoids (hydrogen atoms and crystallized water molecules are omitted for clarity). (b) The cell packing of **1** along the *a* axis.

Table 2. Selected Bond Distances (Å) and Angles (deg) of Complex **1**

Fe(1)−C(1)	1.936(7)	Fe(1)−C(2)	1.933(7)
Fe(1)−C(3)	1.935(8)	Fe(1)−C(4)	1.924(8)
Fe(1)−C(5)	1.938(7)	Fe(1)−N(6)	1.988(5)
C(1)−N(1)	1.145(7)	C(2)−N(2)	1.139(7)
C(3)−N(3)	1.160(8)	C(4)−N(4)	1.155(9)
C(5)−N(5)	1.140(7)	C(9)−N(7)	1.449(9)
Mn(1)−N(1)	2.236(6)	Mn(1)-O(1W)	2.289(4)
Mn(1)−O(1)	1.866(4)	Mn(1)−N(8)	1.977(5)
Mn(1)−O(2)	1.888(4)	Mn(1)−N(9)	1.981(5)
Mn(2)−N(2)	2.222(6)	Mn(2)-O(2W)	2.266(4)
Mn(2)−O(3)	1.880(4)	Mn(2)−N(10)	1.969(5)
Mn(2)−O(4)	1.887(4)	Mn(2)−N(11)	1.979(5)
Mn(1)−N(1)−C(1)	160.0(5)	N(1)−C(1)−Fe(1)	176.7(6)
Mn(2)−N(2)−C(2)	154.3(5)	N(2)−C(2)−Fe(1)	173.5(6)

entities and the oxygen atoms of 5-Brsalen ligands (O(2) and O(4)), coordinated water molecules, and solvent water molecules. Each coordinated water molecule is involved in two H-bonding interactions with D−A separations ranging from 2.843 to 2.976 Å. As shown in Figure 1b, each trinuclear unit is surrounded by six symmetry-related trinuclear units through hydrogen bonds. These abundant hydrogen-bond interactions form a 2D network.

Figure 2. Structure of complex **2** with atom-labeling scheme showing 30% probability thermal ellipsoids (hydrogen atoms and crystallized water molecules are omitted for clarity). Dashed lines represent disordered cyano and 1-methylimidazole groups.
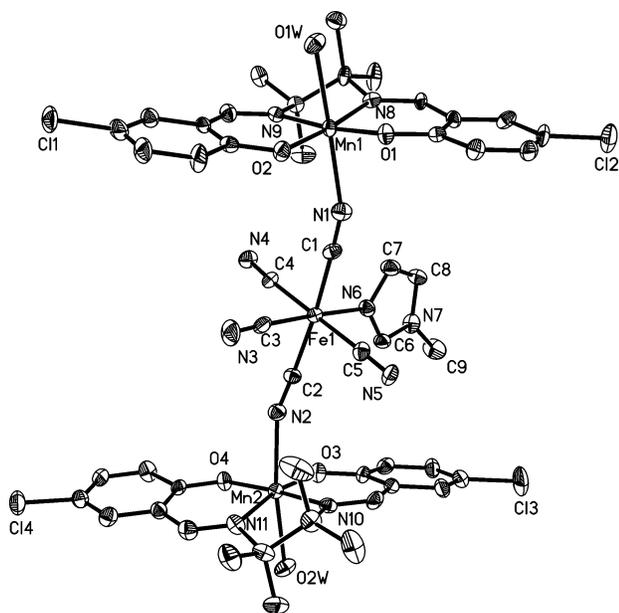
Figure 3. Trinuclear structure of complex **4** with atom-labeling scheme showing 30% probability thermal ellipsoids (hydrogen atoms and crystallized water molecules are omitted for clarity). Complex **5** is isostructural to **4** (Cl is replaced by Br).

nate to the Mn(III) ions in a bent fashion with the Mn−N≡C angles ranging from 149.8(5) to 165.2(6)°. The intramolecular Fe−Mn distances are 5.130 Å for **2**, 5.264, 5.189, 5.150, and 5.158 Å for **3**, 5.307 and 5.244 Å for **4**, and 5.325 and 5.249 Å for **5**.

The coordinated water molecules are involved in hydrogen-bonding interactions with the nonbridging cyano nitrogen atoms and the phenoxo atoms of six neighboring trinuclear units, forming 2D networks as in complex **1**.

Crystal Structure of Complex 6. As shown in Figure 4, complex **6**, {[Et$_4$N][Mn(acacen)Fe(CN)$_5$(1-CH$_3$im)]}$_n$·6nH$_2$O,

exhibits a one-dimensional zigzag chain running along the c axis with $(-Fe-C≡N-Mn-N≡C-)_n$ as the repeating unit. Unlike the 1D analogue, [Et$_4$N]$_2$[Mn(acacen)Fe(CN)$_6$], in which [Fe(CN)$_6$]$^{3-}$ uses two *trans*-cyano ligands to connect two [Mn(acacen)]$^+$ units,[30a] the [Fe(CN)$_5$(1-CH$_3$im)]$^{2-}$ units use two *cis*-cyano groups in the equatorial plane to connect with two [Mn(acacen)] moieties. The Fe−C distances varies from 1.943(8) to 1.949(5) Å, while the Fe−N$_{imidazole}$ bond distance is 1.979(6) Å. The coordination geometry of the Mn(III) ion is also an elongated octahedron, where the equatorial plane is occupied by N$_2$O$_2$ donor atoms of the acacen^{2-} ligand with a Mn(1)−N(1) distance of 1.979(4) Å and a Mn(1)−O(1) distance of 1.902(3) Å, and the two axial positions are occupied by the nitrogen atom N(2) from [Fe(CN)$_5$(1-CH$_3$im)]$^{2-}$ [Mn(1)−N(2) = 2.331(4) Å, N(2)−Mn(1)−N(2B) = 172.8(2)°, B indicates a symmetry operation of x, $0.5 - y$, $-z$].

The bridging cyanide ligands are coordinated to the Mn(III) ion in a bent fashion with an Mn(1)−N(2)−C(7) bond angle of 144.4(4)°, smaller than that (152.6(3)°) in [Et$_4$N]$_2$[Mn(acacen)Fe(CN)$_6$].[30a] The adjacent Fe−Mn distance in the chain is 5.152(5) Å. The disordered Et$_4$N$^+$ cations are located among the Fe(III)−Mn(III) chains and act as charge-balancing cations. In addition, solvent water molecules are also positioned among the chains.

Crystal Structure of Complex 7. In complex **7**, the four equatorial CN$^-$ ligands around the Fe(III) ions coordinate axially to the Mn(III) ions from Mn(saltmen) moieties, while the disordered 1-methylimidazole unit and its opposite CN$^-$ group remains terminal (Supporting Information). As shown in Scheme 2, every two adjacent Mn(saltmen) units are further linked through the Mn−O bonds, which can be widely observed among the [Mn^{III}(saltmen)]$^+$ Schiff base derivatives.[29b,29e,49] Thus, the [−NC−Fe−CN−Mn−O$_2$−Mn−] repeating units lead the complex to a two-dimensional layered structure (Figure 5), with the perchlorate ions and some crystallized water molecules positioned between the layers.

In complex **7**, the Fe(III) ions exhibit a distorted octahedral geometry, with Fe−C bond distances of 1.935(14) and 1.936(8) Å and an Fe−N$_{imidazole}$ bond distance of 1.961(13) Å. The coordination geometry of the Mn(III) ions is elongated octahedral with axial coordination bond distances of Mn(1)−N(1) = 2.197(8) Å and Mn(1)−O(1C) = 2.844(8) Å (C indicates the symmetry operation of $0.5 - x$, $0.5 - y$, $0.5 - z$). The Mn(1)−N(1)−C(1) bond angle of 157.3(7)° shows significant deviation from linearity. The adjacent metal−metal distances are 5.164(8) Å for Fe−Mn and 3.651(8) Å for Mn−Mn.

Another feature of [Fe(1-CH$_3$im)(CN)$_5$]$^{2-}$ lies in the rotation of the imidazole ligand attached to the Fe(III) ion, which is relevant to the electron configuration of Fe(III). The dihedral angle, ϕ, between the imidazole plane and the plane defined by three meridian CN$^-$ ligands, as shown in Scheme 3, can estimate the situation.[45d] For the present seven complexes and the structurally available complex [Mg(1-CH$_3$im)(H$_2$O)$_2$Fe(CN)$_5$(1-CH$_3$im)]·H$_2$O,[45d] the ϕ value ranges from 11.6° for complex **3** to 44.3° for complex **6** (Table 6).
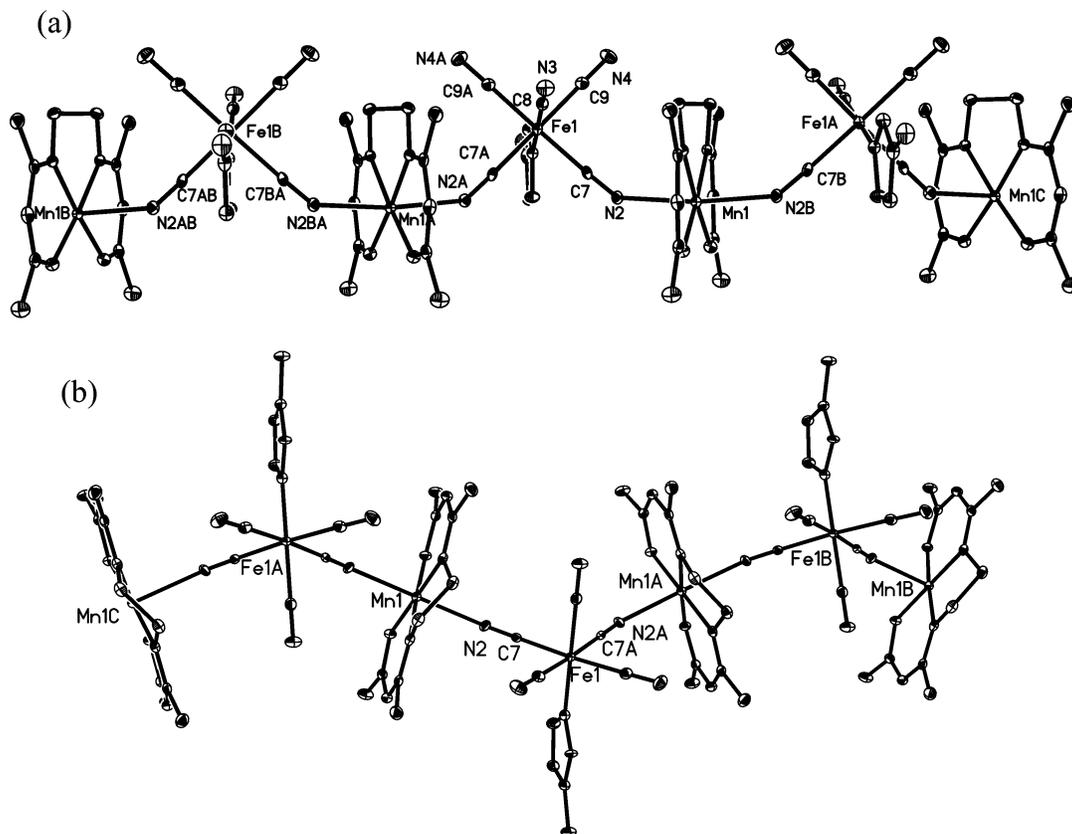
Figure 4. One-dimensional chain propagating along the *c* axis in complex **6** with atom-labeling scheme showing 30% probability thermal ellipsoids (hydrogen atoms, disordered tetraethylammonium cations, and crystallized water molecules are omitted for clarity): (a) 1D zigzag chain showing the bent cyanide bridges and (b) view of the chain emphasizing the orientation of the 1-methylimidazole groups.

Scheme 2
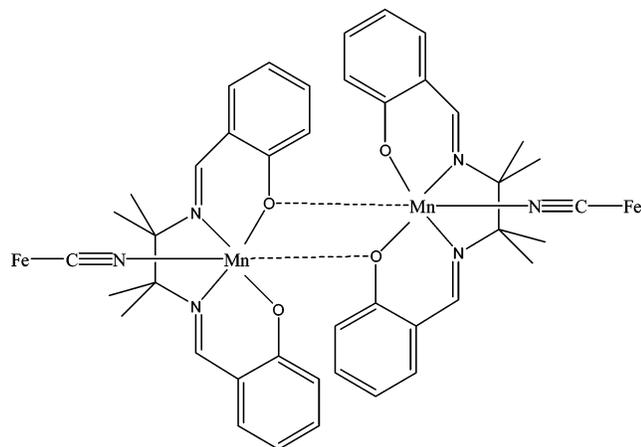
The expectation that the Fe−N(imidazole) bond length is always longer for the smaller ϕ values is basically valid for the present seven complexes.[45d]

Magnetic Properties of Complexes 1−5. The magnetic susceptibility was measured from 5 to 300 K, as shown in Figure 6. The magnetic behaviors of complexes **1−5** are quite similar. The room temperature $\chi_m T$ values are consistent with the presence of high-spin Mn(III) and low-spin Fe(III) ions in **1−5**. Table 7 shows the DC magnetic data for the five trinuclear complexes.

Complexes **1−5** exhibit typical Mn(III)−Fe(III) ferromagnetic interaction with the low-temperature decrease of $\chi_m T$ attributed to intermolecular antiferromagnetic interaction
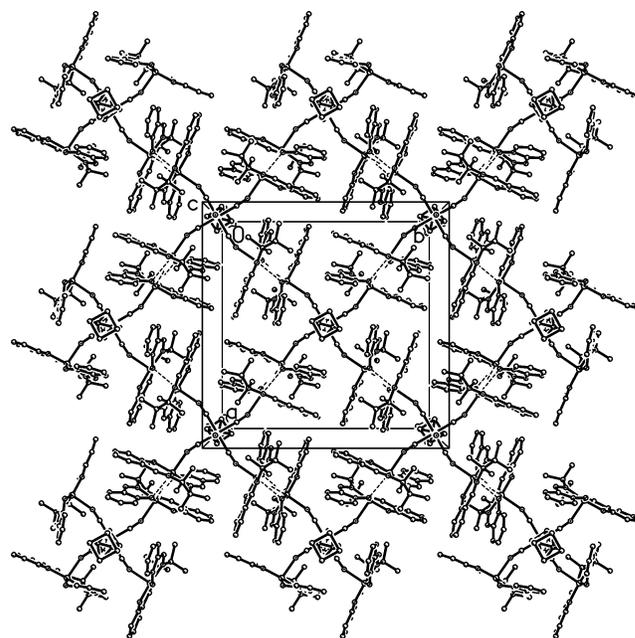
Figure 5. Layered structure of **7** along the *c* axis (hydrogen atoms, perchlorate ions, and water molecules are omitted for clarity).

and the zero-field splitting term of the Mn(III) ion.[29,30,34a,48c,49,50] At low temperatures, both effects result in similar magnetic behavior.

On the basis of the trimeric model, the magnetic susceptibility data for complexes **1−5** can be fitted by the expressions derived from the isotropic exchange spin Hamil-

Scheme 3. Illustration of the ϕ Angle
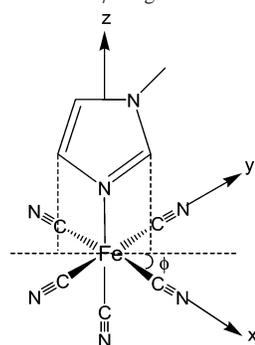
Table 6. Comparison of the Bond Distances for the [Fe(1-CH$_3$im)(CN)$_5$]$^{2-}$-Containing Complexes

	structure	Fe−N(1−CH$_3$im) (Å)	ϕ (deg)	ref
1	trinuclear	1.988(5)	37.1	this work
2	trinuclear	2.039(7)	23.0	this work
3	trinuclear	2.010(6)	11.6	this work
		1.990(5)	33.7	
4	trinuclear	2.008(3)	15.9	this work
5	trinuclear	2.009(3)	17.0	this work
6	1D	1.979(6)	44.3	this work
MgFe	1D	1.950(2)	34.5	45d
7	2D	1.96(1)	42.0	this work

tonian $\hat{H} = -2J\hat{S}_{Fe}(\hat{S}_{Mn(1)} + \hat{S}_{Mn(2)})$, in which we assume equivalent interactions among the central Fe(III) ion and the two Mn(III) ions and neglect the magnetic interaction between the terminal Mn(III) ions (eq 1 in Supporting Information).

If a molecular field term is taken into account, the final magnetic susceptibility can be obtained over the temperature range of 10−300 K. The obtained best-fit parameters are shown in Table 8. If all data down to 5 K were used for the fitting, no satisfactory results could be obtained, which may be caused by the neglect of the zfs (zero-field splitting) effect of Mn(III) during the fitting. The J values are on the order of several cm^{-1}, close to that for the Mn(III)−Fe(III)(CN)$_6$ polynuclear species.[29,48c,49,50]

To include the zfs effect of the ground state ($S_T = 9/2$ for ferromagnetically coupled Mn$_2$Fe species **1−5**), eq 3 can be derived from the spin Hamiltonian $\hat{H} = -2J\hat{S}_{Fe}(\hat{S}_{Mn(1)} + \hat{S}_{Mn(2)}) + D[\hat{S}_z^2 - S(S+1)/3]\delta_{S=9/2}$ (see Supporting Information). It is worth mentioning that this fitting method should be used under the condition that $J \gg |D|$ and the microstates do not couple with the excited spin states (e.g., $S_T = 7/2$; Figure 7, the energy diagram for the trinuclear compounds).[51] Once again, the data in the temperature range of 10−300 K were used for the fitting with the best-fit parameters shown in Table 8. The results show that the J values are slightly larger than that obtained from the former method, and the D values are approximately double the corresponding zJ' values. Figure 6 displays the theoretical curves based on the parameters derived from the latter method. Although the powder magnetic susceptibility data could not unambiguously distinguish the negative or positive sign of D, positive D values could not give satisfactory fitting results for each trinuclear compound. It suggests the presence of negative zfs parameters for complexes **1−5**.
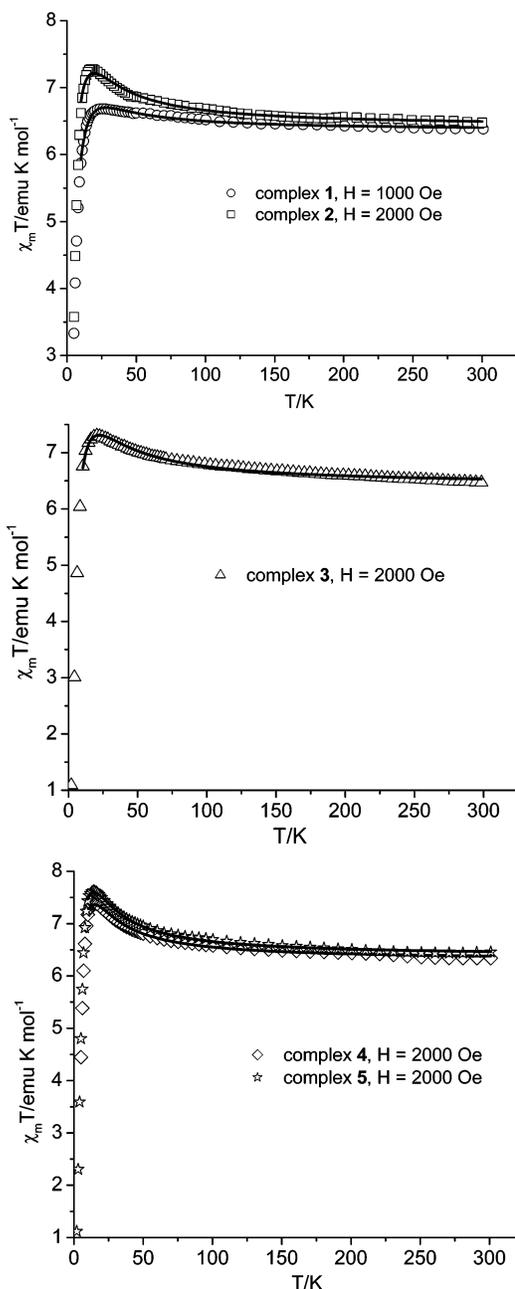
Figure 6. Temperature dependence of $\chi_m T$/Mn$_2$Fe for complexes **1−5**. The solid line represents the calculated values using eq 3.

Table 7. Magnetic Data for the Trinuclear Complexes **1−5**

	room temp $\chi_m T$ (emu K mol^{-1})	Curie constant (emu K mol^{-1})	Weiss constant, θ (K)
1	6.38	6.38	1.24
2	6.49	6.49	2.51
3	6.35	6.03	3.56
4	6.34	6.30	3.23
5	6.46	6.38	3.51

The magnetization curves below 5 K for complexes **1−5** are very similar, showing a slow increase in magnetization at low magnetic fields (<15 kOe) followed by a sharp increase (Supporting Information). This metamagnetic-like behavior reveals that marked intermolecular antiferromagnetic coupling is present in these complexes. Detailed magnetization measurements at 2−6 K and in the applied

Table 8. Comparison of Magnetic Coupling Constants[a]

	ϕ	Mn$-$N$_{cyano}$ (Å)	C$\equiv$N$-$Mn (deg)	J (cm^{-1})	g	zJ' (cm^{-1})	D (cm^{-1})
1	37.1	2.236(6), 2.222(6)	160.0(5), 154.3(5)	4.75(6) 5.92(7)	2.00(1) 2.04(1)	−0.36(1) 0[b]	0[b] −0.88(1)
2	23.0	2.243(5)	149.8(5)	4.98(10) 5.86(11)	2.01(1) 2.04(1)	−0.26(1) 0[b]	0[b] −0.60(1)
3	11.6 33.7	2.221(5), 2.249(5); 2.229(5), 2.298(5)	165.2(5), 156.9(5); 152.8(5), 147.8(5)	6.01(8) 6.68(8)	2.01(1) 2.01(1)	−0.29(1) 0[b]	0[b] −0.67(1)
4	15.9	2.311(3), 2.258(3)	159.7(3), 157.8(3)	4.51(6) 4.95(6)	1.99(1) 1.98(1)	−0.19(1) 0[b]	0[b] −0.43(1)
5	17.0	2.323(3), 2.266(3)	159.4(2), 157.2(3)	4.68(5) 5.10(6)	2.00(1) 2.00(1)	−0.18(1) 0[b]	0[b] −0.40(1)
7	42.0	2.197(8)	157.3(7)	2.34(7)	2.04(2)	0.036(4)	0[b]

[a] Greater than 10 K data have been used for the fitting. [b] The value has been set at zero during the fitting process.
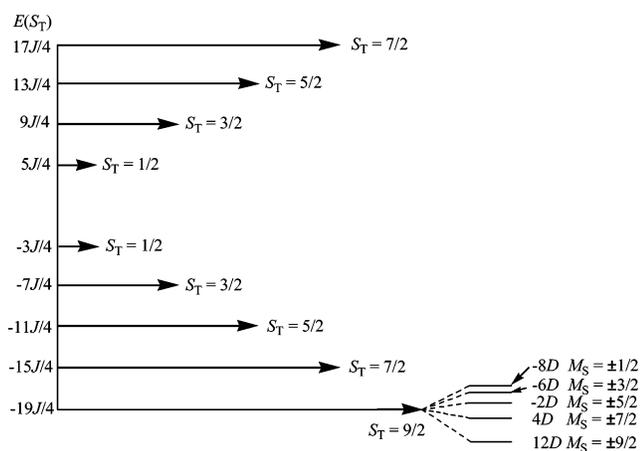
Figure 7. Energy levels in the $|S_T, M_S>$ basis diagram for complexes **1**−**5** (only the zfs effect is considered for the ground state).
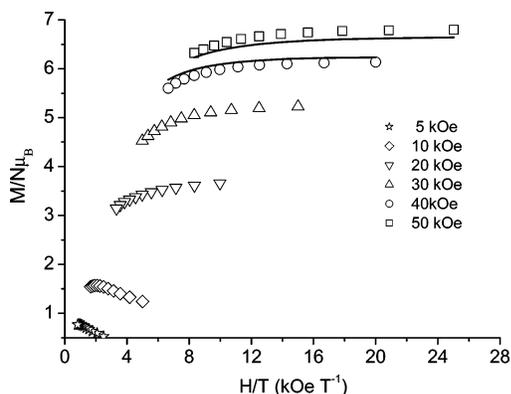
Figure 8. Magnetization vs H/T plot for complex **5** in the range of 2−6 K and 5−50 kOe. The solid lines represent the best fitting results using the Anisofit 2.0 software.

magnetic field of 10−50 kOe for complex **5** show that the isofield lines are not *superimposable*, indicating the presence of appreciable zfs. Significantly, the 5 and 10 kOe magnetization curves show decrease with the increase of H/T, suggesting the presence of an obvious intermolecular antiferromagnetic interaction in **5**. The 40 and 50 kOe data were used to fit using the Anisofit 2.0 program[38d] giving parameters of $g = 1.74$ and $D = -0.70$ cm^{-1} (Figure 8), assuming an $S = 9/2$ ground state and avoiding the intermolecular magnetic coupling effect. Thus, the spin-reversal energy barrier, ΔE, between the $M_S = 9/2$ and $-9/2$ spin states can be calculated to be $\Delta E = 14$ cm^{-1} via $\Delta E = (S^2 - 1/4)|D|$.
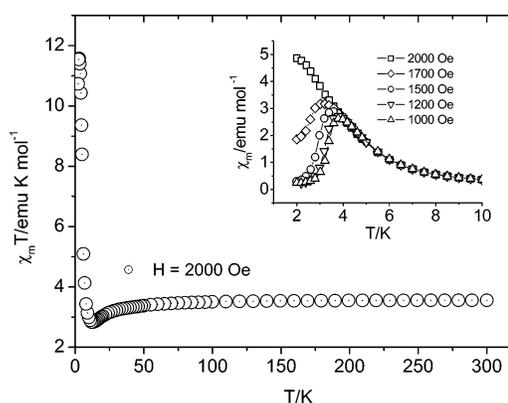
Figure 9. Temperature dependence of $\chi_m T$/MnFe for complex **6**. The inset shows field-cooled magnetization for **6** in different applied magnetic fields.

The temperature dependence of the AC magnetic susceptibility at zero DC and 3 Oe AC magnetic field for complex **5** shows that the out-of-phase AC magnetic susceptibility has nonzero values below 4.0 K and is frequency dependent (Supporting Information). This suggests the presence of slow relaxation of magnetization in complex **5**,[52] consistent with the DC magnetic measurements. However, the signals are considerably weak because of the presence of intermolecular magnetic interaction, precluding any quantitative analysis. It is worth mentioning that two Mn$_2$Fe complexes based on [Fe(CN)$_6$]$^{3-}$ have been proven to be SMMs.[29e,48c]

The above results suggest that trinuclear compounds **1**−**5** exhibit ferromagnetic Mn(III)−Fe(III) coupling, in which an axial zfs effect and appreciable intermolecular antiferromagnetic interaction operate, dominating the low-temperature magnetic behavior.

Magnetic Properties of Complex 6. The magnetic susceptibility was measured from 2 to 300 K under an applied magnetic field of 2000 Oe. A plot of $\chi_m T$ versus T is shown in Figure 9, where χ_m is the magnetic susceptibility per MnFe unit. The $\chi_m T$ value at room temperature is 3.55 emu K mol^{-1}. The $1/\chi_m$ value above 20 K obeys the Curie−Weiss law with a Curie constant of $C = 3.60$ emu K mol^{-1} and a negative Weiss constant of $\theta = -3.23$ K, indicating an antiferromagnetic interaction between the high-spin Mn(III) ions and the low-spin Fe(III) ions through bridging cyanide

(52) Ge, C.-H.; Cui, A.-L.; Ni, Z.-H.; Jiang, Y.-B.; Zhang, L.-F.; Ribas, J.; Kou, H.-Z. *Inorg. Chem.* **2006**, *45*, 4883.
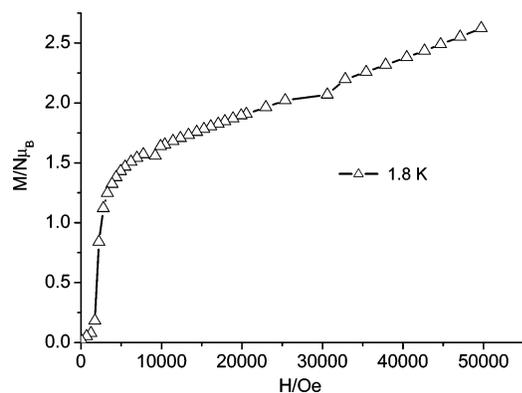
Figure 10. Field dependence of magnetization for complex **6**. The solid line is a guide for the eye.

Figure 11. Temperature dependence of $\chi_m T/Mn_4Fe$ for complex **7**. The solid line represents the calculated values. The inset shows the field-cooled magnetization (□), the zero-field-cooled magnetization (▲), and the remanent magnetization (◇) for **7**.

Figure 12. Field dependence of magnetization at 2 K for complex **7**. The solid lines are guides for the eye. The inset shows the hysteresis loop for **7** at 2 K.

groups. When the temperature is lowered, $\chi_m T$ decreases gradually to reach a minimum of 2.83 emu K mol^{-1} at 12.0 K, then increases abruptly to reach a maximum of 11.57 emu K mol^{-1} at 3.0 K, and finally decreases again to 10.73 emu K mol^{-1} at 2.2 K. The presence of the abrupt increase of $\chi_m T$ suggests the onset of magnetic ordering.

To confirm the magnetic phase transition at low temperature, we measured the FCM (field-cooled magnetization) curve under different magnetic fields in the temperature range of 2−10 K, and the results are shown in the inset of Figure 9. Below 1700 Oe, the FCM curves show a peak at ∼4 K, which can be considered as the antiferromagnetic phase transition temperature (T_N). This peak disappears when the curve was measured at 2000 Oe, suggesting a typical metamagnetic behavior of this antiferromagnet and the range of 1700−2000 Oe of the critical field (H_c).

The metamagnetic behavior was further characterized by the measurements of field-dependent magnetization at 1.8 K. Figure 10 shows that the curve has the sigmoidal shape expected for a metamagnet: the magnetization first increases slowly with the external field because of antiferromagnetic interchain interactions and then increases sharply, showing a phase transition to a ferrimagnetic state. The critical field at 2 K is about 1700 Oe, corresponding to the FCM results. When the field is increased further, the magnetization reaches 2.4 $N\beta$ at the highest measured field (50 kOe) and continues to increase, indicating that saturation (expected value of 3 $N\beta$ for $S_T = S_{Mn} - S_{Fe} = 3/2$) has not yet been achieved. Such behavior can be often observed in [Mn(SB)]$^+$-containing compounds[29] because of the large zero-field splitting of the Mn(III) ions.

Magnetic Properties of Complex 7. The magnetic susceptibility was measured from 2 to 300 K under an applied magnetic field of 2000 Oe, as shown in Figure 11. The $\chi_m T$ value per Mn$_4$Fe at room temperature, 12.33 emu K mol^{-1}, is very similar to the spin-only value of 12.375 emu K mol^{-1} expected for the magnetically dilute five-spin system (S_{Fe}, S_{Mn}, S_{Mn}, S_{Mn}, S_{Mn}) = (1/2, 2, 2, 2, 2). When the temperature is lowered, $\chi_m T$ increases smoothly and then sharply without a minimum to reach a maximum as high as 41.68 emu K mol^{-1} at 5.0 K, strongly suggestive of the occurrence of a three-dimensional magnetic ordering. The magnetic susceptibilities obey the Curie−Weiss law with a positive Weiss
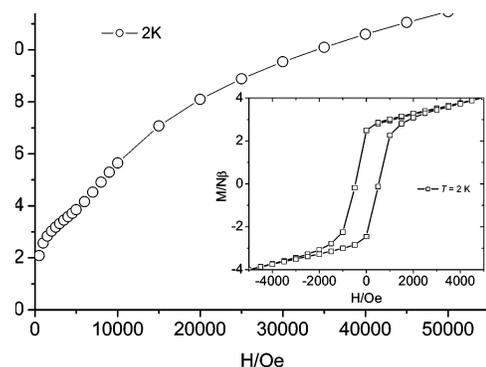
constant $\theta = 5.64$ K and a Curie constant $C = 12.1$ emu K mol^{-1}, indicating an overall ferromagnetic interaction between Mn(III) ions and Fe(III) ions through bridging cyanide groups.

To confirm the magnetic phase transition, the FCM and ZFCM curve was measured using the usual procedure. An abrupt increase in the magnetization is observed at ∼4.8 K, where the remanent magnetization vanishes (inset of Figure 11). These characteristics indicate that complex **7** exhibits a long-range ferromagnetic ordering at 4.8 K. This T_c value is comparable to that (4.5 K) of the isostructural [Mn(saltmen)]$_4$-[Fe(CN)$_6$]ClO$_4$.[29b]

The magnetization curve at 2 K (Figure 12) shows a rapid increase in M at low magnetic field, typical of a ferromagnet. At 50 kOe, the magnetization value is ∼12 $N\beta$, lower than the theoretical value of 17 $N\beta$ for a ferromagnetically coupled Mn$_4$Fe system. Once again, the zfs effect of Mn(III) should account for this phenomenon. Hysteresis at 2 K is evident with the coercive field of about 500 Oe and the remanent magnetization of 2.5 $N\beta$ (inset of Figure 12). These data suggest that complex **7** is a soft ferromagnet.

To evaluate the magnitude of the intramolecular magnetic coupling, we tried to fit the magnetic susceptibilities with an approximate model. The structural data show that in complex **7** there are two different magnetic coupling pathways, cyano bridges and phenoxo bridges. The layers can be schematically illustrated in Scheme 4, where J is for

Scheme 4. Two Magnetic Coupling Pathways in the Layer of **7**

——— cyano bridge ------ phenoxo bridge

Situation 1: d_{xz}-d_{z^2} orbital overlap of two metal ions.

Situation 2: dihedral angle is zero favoring d_{xz}-d_{xz} orbital overlap of two metal ions.

Situation 3: dihedral angle is nonzero unfavoring d_{xz}-d_{xz} orbital overlap of two metal ions.

Figure 13. Different magnetic exchange situations with bent Fe−C≡N−Mn linkages.
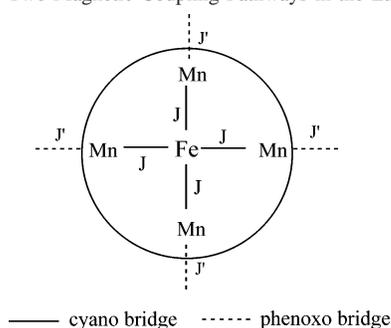
the cyano bridges and J' for phenoxo ones. It has been reported by Miyasaka et al. that $|J| \gg |J'|$,[29b,29e,29h] and the 2D layer can be therefore described as weakly interacting Mn_4Fe pentanuclear units.

On the basis of above considerations, the magnetic data were fitted to the van Vleck equation for the pentanuclear unit derived from an isotropic exchange Hamiltonian $\hat{H} = -2J\hat{S}_{Fe}(\hat{S}_{Mn1} + \hat{S}_{Mn2} + \hat{S}_{Mn3} + \hat{S}_{Mn4})$.[29c,50] The magnetic coupling via the phenoxo bridges was treated as intermolecular term using the mean-field method. The final molar magnetic susceptibility (χ_m) is in the form of $\chi_m = \chi_p/[1 - \chi_p(2zJ'/Ng^2\beta^2)]$, where χ_p is for the Mn_4Fe pentanuclear unit, J' is the coupling constant between the pentanuclear units, and $z = 4$, the number of nearest Mn_4Fe neighbors. The best-fit parameters based on the data above 10 K are $J = 2.34$ cm^{-1}, $zJ' = 0.036$ cm^{-1}, $g_{Mn} = 1.99$, and $g_{Fe} = 2.04$. The calculated solid line shown in Figure 11 agrees well with the experimental values. The calculated J value is comparable to that (1.4 cm^{-1}) for the pentanuclear compound [Mn(salpn)-(CH$_3$OH)]$_4$[Fe(CN)$_6$]ClO$_4$·9H$_2$O (salpn^{2-} = N,N'-propyl-enebis(salcylideneiminato) dianion) reported by Liao et al.[50] The positive J' value suggests the presence of ferromagnetic Mn(III)−Mn(III) coupling through the phenoxo bridges.

It it noteworthy that the ϕ values for the present complexes cover a wide range (11.6−44.3°), which should affect the electronic configuration of Fe(III) in [Fe(1-CH$_3$im)(CN)$_5$]$^{2-}$.[45d] When ϕ is equal to 45°, the d_{xz} and d_{yz} orbitals are degenerate, whereas other angles cause d_{xz} to be a little higher in energy if the xz plane is used to evaluate the ϕ value (Scheme 3). For the present [Fe(1-CH$_3$im)(CN)$_5$]$^{2-}$ complexes, the electronic configuration of low-spin Fe(III) is unambiguously $d_{xy}^2d_{yz}^2d_{xz}$, which is different from that in [Fe(CN)$_6$]$^{3-}$. In the case of octahedral [Fe(CN)$_6$]$^{3-}$, the $d_{xy}d_{yz}d_{xz}$ orbitals are degenerate, and the unpaired electron is equally populated on the three orbitals.

Most cyanide-bridged Mn(III)−Fe(III) complexes reported previously exhibit ferromagnetic interactions with few exceptions. This work affords five more ferromagnetically coupled examples, further revealing that ferromagnetic Mn^{III}−Fe^{III} coupling is more usual. This fact seems to be contrary to the predictions according to the strict orbital orthogonality theory because of the presence of magnetic orbital overlap between t_{2g} orbitals ($d_{xy}d_{yz}d_{xz}$) of high-spin Mn(III) and low-spin Fe(III) (d_{xz}). However, the frequent bending of the Mn−N≡C−Fe linkages and the rotation of the x and z axes for Mn(III) compared with the xz plane for
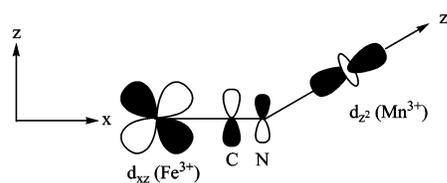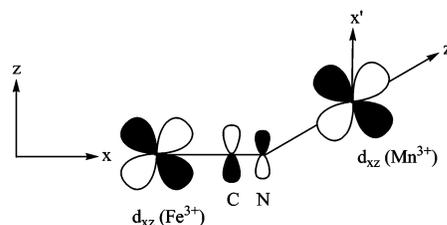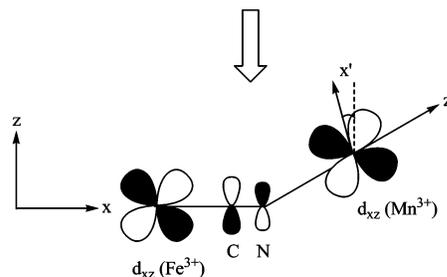
Fe(III) should reduce the overlap and therefore weaken the antiferromagnetic contribution according to Goodenough−Kanamori rules (Figure 13).[29b,53] Consequently, overall ferromagnetic coupling occurs in complexes **1**−**5** and **7**. For antiferromagnetically coupled complex **6**, the bending of the bridging linkages and the rotation of the xz plane for Mn(III) are present. However, the smallest Mn−N≡C bond angle in **6** may be responsible for the AF behavior. In addition to the reduction of antiferromagnetic coupling, the bent Mn−N≡C bond angle is unfavorable for the ferromagnetic coupling between d_{z^2} of Mn(III) and d_{xz} of Fe(III) (situation 1 in Figure 13), and below a certain bond angle the overall magnetic coupling becomes antiferromagnetic.

Conclusions

We first investigated the [Fe(1-CH$_3$im)(CN)$_5$]$^{2-}$ building block for the construction of polynuclear or polymeric bimetallic Mn(III)−Fe(III) complexes. The ferromagnetic or antiferromagnetic Mn(III)−Fe(III) coupling has been attributed to the bending of the Mn−N≡C−Fe linkage and the nonplanarity of the xz planes of Mn(III) and Fe(III). Future work involves the synthesis of cyanide-bridged M(II)−Fe(III) complexes (M = Mn, Ni, Cu) using the versatile [Fe(1-CH$_3$im)(CN)$_5$]$^{2-}$ building block to gain a magnetostructural correlation.[54]

(53) Goodenough, J. B. *Phys. Rev.* **1955**, *100*, 564. Kanamori, J. *J. Phys. Chem. Solids* **1959**, *10*, 87.
(54) Zhang, Y.-Q.; Luo, C.-L.; Yu, Z. *New J. Chem.* **2005**, *29*, 1285.

Supporting Information Available: Crystallographic data in CIF format, selected bond distances and angles for complex **3**, structures for complexes **3**, **5**, and **7**, field dependence of magnetization for complexes **1**−**5**, magnetic fit equations for trinuclear Mn_2Fe systems, and temperature dependence of AC magnetic susceptibility at zero DC magnetic field. This material is available free of charge via the Internet at http://pubs.acs.org.

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