6004 *Inorg. Chem.* **1996,** *35,* 6004−6008

Magnetic Properties of a One-Dimensional Ferromagnet Containing a Mn(III)−NC−Fe(III) Linkage: Synthesis and Crystal Structure of a Chainlike [Mn(acacen)Fe(CN)$_6$]$_n$$^{2n-}$ Polyanion

Nazzareno Re,[†] Emma Gallo,[‡] Carlo Floriani,*,[‡] Hitoshi Miyasaka,[§] and Naohide Matsumoto*,[§]

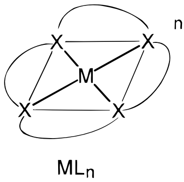
Dipartimento di Chimica, University of Perugia, via Elce di Sotto 8, 06100 Perugia, Italy, Institut de Chimie Minérale et Analytique, University of Lausanne, BCH, CH-1015 Lausanne, Switzerland, and Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan

Received May 16, 1996[⊗]

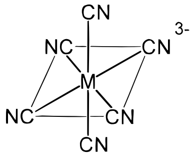
A one-dimensional compound with a Mn(III)−NC−Fe(III) linkage of the formula of [NEt$_4$]$_2$[Mn(acacen)][Fe(CN)$_6$] (NEt$_4$ = tetraethylammonium, acacen = *N,N′*-ethylenebis(acetylacetonylideneaminato)) has been prepared by the assembly reaction of [Mn(acacen)Cl] and [NEt$_4$]$_3$[Fe(CN)$_6$] in ethanol/2-propanol. The compound crystallizes in the orthorhombic space group *Pnma* with the cell dimensions of a = 17.415(5) Å, b = 19.79(1) Å, c = 11.471(4) Å, and Z = 4. The compound assumes a one-dimensional snaky-chain structure consisting of (−Mn−NC−Fe−CN−)$_n$ repeating units with dimensions of Fe−C = 1.952(4) Å, Mn−N = 2.316(4) Å, Mn−N−C = 152.6(3)°, Fe−C−N = 177.1(4)°, in which the Fe ion is positioned at the inversion center, the [Mn(acacen)] moiety lies on a mirror plane, and the adjacent one-dimensional chains run like a snake along the b axis with the same phase. On lowering of the temperature, the effective magnetic moment per FeMn increases gradually from 5.05 μ_B at room temperature and then abruptly below ca. 20 K to 15.5 μ_B at 1.9 K, indicating that the one-dimensional chain is a ferromagnetic chain due to an intrachain ferromagnetic coupling between Mn(III) and Fe(III) ions through the bridging CN$^-$ group. The FCM curve (field-cooled magnetization) under 1 Oe showed a spontaneous magnetization below 2.5 K. The magnetization vs H up to 55 kOe at 1.9 K showed an extremely large zero-field susceptibility, indicating that the compound is a ferromagnet due to a weak interchain ferromagnetic coupling.

Introduction

Major attention is currently being devoted to the molecular design of extended structures with target magnetic properties.[1] Apart from the interest in prussian-blue solid-state materials,[2] there is increasing research emphasis on macromolecules and extended-array bimetallic compounds assembled from hexacyanometalate building blocks and metal ions with polydentate ligands.[3] The building principle can be exemplified by the various possible assembling modes which can occur between the bulding blocks **A** and **B**, the connectivity between the two being ensured by the cyanide anion functioning as a bridging ligand.



ML$_n$
A



[M(CN)$_6$]$^{3-}$
B

Depending on the nature of **A**, the constituents **A** and **B** can give rise to mono-, bi-, or tridimensional frameworks, as function of (i) the geometrical propinquity of the available coordination sites on M, (ii) the coordination number of M, (iii) the steric hindrance of the polydentate/macrocyclic ligand around M, and (iv) the oxidation state of M determining the charge of the repeating unit in the polymeric framework. In this respect, the countercation or counteranion disposition between the oligomeric/polymeric unit may be crucial for the topology of the solid.

The reaction between [Mn(BS)] [BS = salen-substituted, salen = *N,N′*-ethylenebis(salicylideneaminato) dianion] and [Fe(CN)$_6$]$^{3-}$, fitting in the assembling scheme mentioned above, gave rise to two-dimensional layer structures, having meta-, ferri-, and ferromagnetic properties.[3a,b] The nature of the Mn-

---

[†] University of Perugia.

[‡] University of Lausanne.

[§] Kyushu University.

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.

(1) (a) Kahn, O. *Molecular Magnetism,* VCH: Weinheim, Germany, 1993. (b) *Magnetic Molecular Materials*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; NATO ASI Series E, Vol. 198; Kluwer: Dordrecht, The Netherlands. (c) Iwamura, H.; Miller, J. S. Proceedings of the Symposium on the Chemistry and Physics of Molecular Based Magnetic Materials. *Mol. Cryst. Liq. Cryst.* **1993**, 232−233. (d) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *106*, 399. (e) Caneschi, A.; Gatteschi, D.; Sessoli, R.; Rey, P. *Acc. Chem. Res.* **1989**, *22*, 392. (f) Kahn, O. *Struct. Bonding* **1987**, *67*, 89. (g) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201. (h) Chen, C.-T.; Suslick, K. S. *Coord. Chem. Rev.* **1993**, *128*, 293.

(2) (a) Gadet, V.; Mallah, T.; Castro, I.; Veillet, P.; Verdaguer, M. *J. Am. Chem. Soc.* **1992**, *114*, 9213. (b) Ito, A.; Suenaga, M.; Ono, K. *J. Chem. Phys.* **1968**, *48*, 3597. (c) Mallah, T.; Thiebault, S.; Verdaguer, M.; Veillet, P. *Science* **1993**, *262*, 1555. (d) Knoeppel, D. W.; Shore, S. G. *Inorg. Chem.* **1996**, *35*, 1747. (e) Entley, W. R.; Girolami, G. S. *Science* **1995**, *268*, 397. (f) Dunbar, K. R.; Heintz, R. A. *Prog. Inorg. Chem.* **1996**, *45*, in press.

(3) (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) Ohba, M.; Maruono, N.; Okawa, H.; Enoki, T.; Latour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11566. (d) Mallah, T.; Auberger, C.; Verdaguer, M.; Veillet, P. *J. Chem. Soc., Chem. Commun.* **1995**, 61. (e) Ohba, M.; Okawa, H.; Ito, T.; Ohto, A. *J. Chem. Soc., Chem. Commun.* **1995**, 1545.

S0020-1669(96)00556-3 CCC: $12.00

(III)−salen-based building block, however, did not enter the one- or three-dimensional extended structures.

We report here how the properties associated with the [Mn(acacen)]$^+$ fragment [acacen = *N*,*N*′-ethylenebis(acetylacetonylideneaminato) dianion], where the metal can easily achieve hexacoordination, and the stoichiometry of the reaction with $[Fe(CN)_6]^{3-}$ self-adjusting at a 1:1 molar ratio gave rise to a ferromagnetic one-dimensional network. A particular role is played by the countercation $[NEt_4]^+$.

Experimental Section

Physical Measurements. Elemental analyses for C, H, and N were performed at the Elemental Analysis Service Center of Kyushu University. Manganese and iron analyses were made on a Shimadzu AA-680 atomic absorption/flame emission spectrophotometer. Infrared spectra were measured on KBr disks with JASCO IR-810 and Shimadzu FTIR-8600 spectrophotometers. Magnetic susceptibilities, field dependences of magnetization up to 55 kOe, and field-cooled magnetization measurements under 1 Oe were obtained using a MPMS5 SQUID susceptometer (Quantum Design Inc.). Corrections were applied for diamagnetism calculated from Pascal's constants.[4] Effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the magnetic susceptibility per formula unit.

X-ray Data Collection and Reduction and Structure Determination of 3. Single crystals were obtained by the slow crystallization described in section on the synthetic procedure. A crystal with the dimensions 0.2 × 0.2 × 0.3 mm was used for the X-ray diffraction study. All measurements were made on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) and a 12 kW rotating-anode generator. The data were collected at a temperature of 20 ± 1 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 50.0° at a scan speed of 16.0°/min (in ω). The intensities of three representative reflections were measured after every 150 reflections. Over the course of the data collection, the standard reflections were monitored and the decay polynomial corrections were applied. An empirical absorption correction based on azimuthal scans of several reflections was applied. The data were corrected for Lorentz and polarization effects. A more detailed procedure of the data collection can be seen in our previous paper.[3b]

The structure was solved by direct methods[5] and expanded using Fourier techniques.[6] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included. Full-matrix least-squares refinement based on observed reflections ($I > 3.00\sigma(I)$) were employed, where the unweighted and weighted agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma|w(|F_o| - |F_c|)^2/\Sigma|w|F_o|^2]^{1/2}$ were used and the weights were $1/(\sigma^2(F_o))$. Neutral atom scattering factors were taken from Cromer and Waber.[7] Anomalous-dispersion effects were included in F_c; the values were those of Creagh and McAuley.[8] All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corp.[9] Crystal data and details of the structure determinations are summarized in Table 1. Positional parameters for non-hydrogen atoms are given in Table 2.

Table 1. Experimental Data for the X-ray Diffraction Studies of Crystalline **3**

empirical formula	$C_{34}H_{58}FeMnNO_2$	Z	4
		fw	749.68
a (Å)	17.415(5)	space group	*Pnma* (orthorhombic)
b (Å)	19.79(1)	λ (Å)	0.710 69
c (Å)	11.471(4)	ρ_{calcd} (g cm^{-3})	1.260
α (deg)	90	μ (cm^{-1})	7.28
β (deg)	90	R^a	0.042
γ (deg)	90	R_w^b	0.043
V (Å^3)	3952(2)		

[a] $R = \Sigma|\Delta F|/\Sigma|F_o|$. [b] $R_w = [\Sigma|w(|F_o| - |F_c|)^2/\Sigma|w|F_o|^2]^{1/2}$.

Table 2. Atomic Positional Parameters and Isotropic Temperature Factors (Å^2) for **3**

atom	*x*	*y*	*z*	*B*(eq)
Fe(1)	0.000000	0.0	0.00000	2.49(2)
Mn(1)	−0.10006(5)	$-^1/_4$	−0.0016(1)	2.58(2)
O(1)	−0.1973(2)	$-^1/_4$	0.0759(4)	3.1(1)
O(2)	−0.1479(2)	$-^1/_4$	−0.1510(4)	2.9(1)
N(1)	−0.0439(3)	$-^1/_4$	0.1472(5)	3.6(1)
N(2)	0.0037(3)	$-^1/_4$	−0.0721(5)	2.9(1)
N(3)	−0.0935(2)	−0.1332(2)	0.0084(4)	3.51(9)
N(4)	−0.1406(2)	0.0896(2)	0.0616(3)	3.8(1)
N(5)	0.0453(2)	−0.0226(2)	0.2593(4)	5.2(1)
N(6)	0.1794(2)	−0.0142(2)	0.6093(3)	3.08(9)
C(1)	−0.2914(3)	$-^1/_4$	0.2203(6)	4.2(2)
C(2)	−0.2085(3)	$-^1/_4$	0.1868(6)	2.9(2)
C(3)	−0.1533(4)	$-^1/_4$	0.2699(6)	4.0(2)
C(4)	−0.0727(4)	$-^1/_4$	0.2497(6)	3.4(2)
C(5)	−0.0203(4)	$-^1/_4$	0.3583(7)	6.4(3)
C(6)	0.0354(4)	−0.2776(4)	0.1274(8)	3.6(2)
C(7)	0.0635(3)	$-^1/_4$	0.0153(6)	3.6(2)
C(8)	0.1026(4)	$-^1/_4$	−0.2236(6)	4.3(2)
C(9)	0.0195(4)	$-^1/_4$	−0.1841(6)	3.4(2)
C(10)	−0.0376(4)	$-^1/_4$	−0.2716(6)	3.7(2)
C(11)	−0.1152(4)	$-^1/_4$	−0.2524(6)	3.2(2)
C(12)	−0.1714(4)	$-^1/_4$	−0.3526(6)	4.1(2)
C(13)	−0.0606(2)	−0.0830(2)	0.0060(4)	2.9(1)
C(14)	−0.0885(2)	0.0562(2)	0.0406(4)	2.8(1)
C(15)	0.0280(2)	−0.0132(2)	0.1644(4)	3.3(1)
C(16)	0.1142(3)	−0.0654(2)	0.6224(4)	3.8(1)
C(17)	0.1086(3)	−0.1174(3)	0.5264(5)	5.5(2)
C(18)	0.1698(3)	0.0287(2)	0.5002(4)	4.0(1)
C(19)	0.1006(3)	0.0753(3)	0.5020(5)	5.6(1)
C(20)	0.1785(3)	0.0297(2)	0.7188(4)	3.6(1)
C(21)	0.2402(3)	0.0816(3)	0.7262(5)	5.6(2)
C(22)	0.2559(3)	−0.0506(3)	0.5979(4)	3.8(1)
C(23)	0.2755(3)	−0.0971(3)	0.6975(4)	4.7(1)

General Procedures and Materials. All chemicals and solvents used for the syntheses were reagent grade. The quadridentate Schiff base ligand H_2acacen[10] and [Mn(acacen)Cl][11] were prepared according literature methods. $[NEt_4]_3[Fe(CN)_6]$ was prepared at room temperature.[12] However, because of its tendency to decompose on irradiation, crystallization was performed in the dark.

Synthesis of 3, $[NEt_4]_2$[Mn(acacen)]$[Fe(CN)_6]$. To a solution of [Mn(acacen)Cl], **1** (0.31 g, 1.0 mmol), in ethanol (20 mL) was added a solution of $[NEt_4]_3[Fe(CN)_6]$, **2** (0.60 g, 1.0 mmol), in ethanol (5 mL). The resulting solution was filtered, to the filtrate was added 30 mL of 2-propanol, and the mixture was allowed to stand for 3 days in dark. Rhombic brown crystals formed and were collected by filtration, washed with 2-propanol, and dried *in vacuo*. Anal. Calcd for **3**, $C_{34}H_{58}FeMnN_{10}O_2$: C, 54.47; H, 7.80; N, 18.68; Mn, 7.33; Fe, 7.45. Found; C, 54.29; H, 7.78; N, 18.55; Mn, 7.28; Fe, 6.71. IR(KBr): ν[C=N(imine)] 1601 cm^{-1}; ν[C−N(cyanide)] 2124 cm^{-1}. Mp: >300 °C.

---

(4) Boudreaux, E. A.; Mulay, L. N. In *Theory and Applications of Molecular Paramagnetism*; Wiley: New York, 1976; pp 491−495.

(5) SAPI91: Fan Hai-Fu. *Structure Analysis Programs with Intelligent Control*; Rigaku Corp.: Tokyo, 1991. MULTAN88: Debaerdemaeker, T.; Germain, G.; Main, P.; Refaat, L. S.; Tate, C.; Woolfson, M. M. *Computer program for the automatic solution of crystal structures from X-ray diffraction data*; University of York: York, U.K., 1988. SHELXS86: Sheldrick, G. M. *A program for X-ray crystal structure determination*; University of Cambridge: Cambridge, U.K., 1986.

(6) DIRDIF92: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system. Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1992.

(7) Creagh, D. C.; McAuley, W. J. *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer: Boston, 1992; Vol. C, Table 4.2.6.8, pp 219−222. Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.2A.

(8) Creagh, D. C.; Hubbel, J. H. *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer: Boston, 1992; Vol. C, Table 4.2.4.3, pp 200−206.

(9) teXsan: *Crystal Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985, 1992.

(10) McCarthy, P. J.; Hovey, R. J.; Ueno, K.; Martell, A. E. *J. Am. Chem. Soc.* **1955**, *77*, 5820.

(11) Boucher, L. J.; Day, V. W. *Inorg. Chem.* **1977**, *16*, 1360.

(12) Mascharak, P. K. *Inorg. Chem.* **1986**, *25*, 245.

Scheme 1

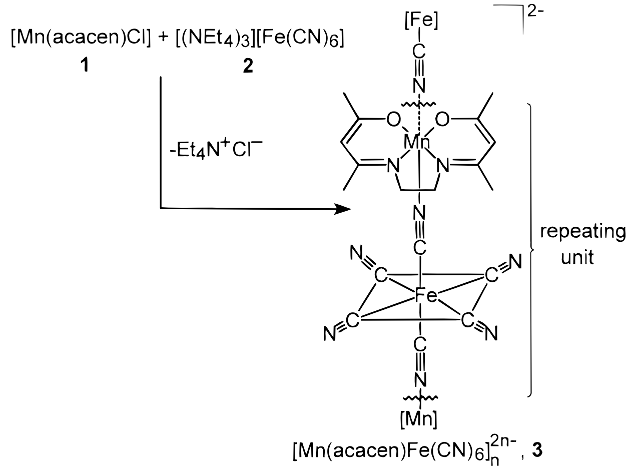


Table 3. Relevant Bond Distances (Å) and Angles (deg) of **3** with Estimated Standard Deviations in Parentheses

Fe−C(13)	1.953(4)	N(5)-C(15)	1.145(5)
Fe−C(14)	1.956(5)	N(6)-C(16)	1.529(5)
Fe−C(15)	1.965(5)	N(6)-C(18)	1.522(5)
Mn−O(1)	1.912(4)	N(6)-C(20)	1.527(5)
Mn−O(2)	1.906(4)	N(6)-C(22)	1.522(5)
Mn−N(1)	1.967(5)	C(1)-C(2)	1.494(8)
Mn−N(2)	1.980(5)	C(2)-C(3)	1.354(8)
Mn−N(3)	2.316(4)	C(3)-C(4)	1.422(8)
O(1)-C(2)	1.286(7)	C(4)-C(5)	1.544(9)
O(2)-C(11)	1.295(7)	C(6)-C(7)	1.48(1)
N(1)-C(4)	1.278(8)	C(8)-C(9)	1.516(8)
N(1)-C(6)	1.504(8)	C(9)-C(10)	1.413(9)
C(11)-C(12)	1.510(8)	C(10)-C(11)	1.369(8)
N(2)-C(7)	1.446(7)	C(16)-C(17)	1.510(6)
N(2)-C(9)	1.313(8)	C(18)-C(19)	1.517(6)
N(3)-C(13)	1.149(5)	C(20)-C(21)	1.488(6)
N(4)-C(14)	1.148(5)	C(22)-C(23)	1.507(6)
Mn−N(3)-C(13)	152.6(3)	Fe−C(13)-N(3)	177.1(4)
N(3)-Mn−N(3)*	172.0(2)		

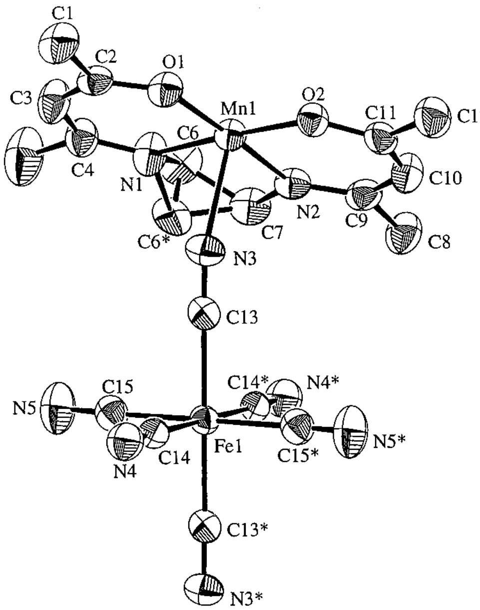


Figure 1. ORTEP drawing of the anion $[Mn(acacen)][Fe(CN)_6]^{2-}$ with the atom-numbering scheme for the unique atoms, showing 50% probability ellipsoids.

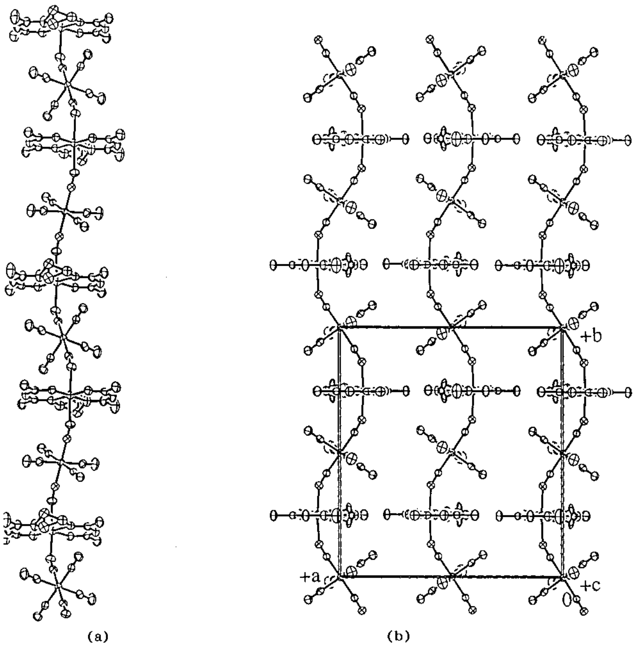


Figure 2. (a) One-dimensional chain structure of consisting of $(-Mn-NC-Fe-CN-)_n$ as the repeating unit. (b) Stacking of the adjacent one-dimensional snaky chains running along the *b* axis.

Results and Discussion

Synthesis and Characterization. The reaction between **1** and **2** was carried out in ethanol/2-propanol and always gave a 1:1 molar ratio product, **3**, regardless of the reactant ratio used. The use of the $[EtN_4]^+$ countercation instead of K^+ allowed the reaction to be carried out in organic solvents in conjunction with better crystallization products. A further consequence of using the $[EtN_4]^+$ cation is that it results in only very weak interchain interactions.

Structural Study. An ORTEP view of the repeating anion $[Mn(acacen)Fe(CN)_6]^{2-}$ with the atom numbering scheme of the unique atoms is shown in Figure 1, while the relevant bond distances and angles are reported in Table 3. Iron occupies the inversion centers. The [Mn(acacen)] moiety lies on a mirror plane and thus is crystallographically required to be in a plane. This is why C(6) is disordered, since the five-membered chelate ring generally assumes a gauche conformation. Because the Fe ion is positioned at the inversion center and the Mn ion lies on a mirror plane, the two axial coordination sites on each metal are equivalent with regard to bond distance. The compound assumes a one-dimensional twisted-chain structure running along the *b* axis, having $(-Fe-CN-Mn-NC-)_n$ as the repeating unit (Figure 1) [Fe−C(13) = 1.952(4), N(3)−C(13) = 1.148(5), Mn−N(3) = 2.316(4), Mn−N(3)−C(13) = 152.6(3)° = Fe−C(13)−N(3) = 177.1(4)°, and N(3)−Mn−N(3)* = 172.0(2)°]. The coordination geometry of the Mn ion is described as an elongated square bipyramid, where the basal plane is occupied by N_2O_2 donor atoms of acacen [Mn−N(1) = 1.967(5), Mn−N(2) = 1.980(5), Mn−O(1) = 1.912(4), and Mn−O(2) = 1.906(4) Å] and the two axial positions are occupied by the nitrogen atom N(3) from $[Fe(CN)_6]$ [Mn−N(3) = 2.316(4) Å]. The average Mn−O and Mn−N distances within the [Mn(acacen)] moiety are shorter than those observed in $[Mn^{II}(acacen)]$ derivatives[13] and rather close to those of the parent compound [Mn(acacen)Cl].[11] The structural parameters related to the Mn−N≡C−Fe skeleton [Mn−N = 2.316(4) Å, Mn−N−C = 152.6(3)°] are averages of those observed in the [Mn(salen-substituted)]$^+$/$[Fe(CN)_6]^{3-}$ adducts.[3a,b]

Figure 2 shows the stacking of the neighboring chains. The adjacent chains run like a snake along the *b* axis with the same

---

(13) Gallo, E.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1995**, *14*, 2156.

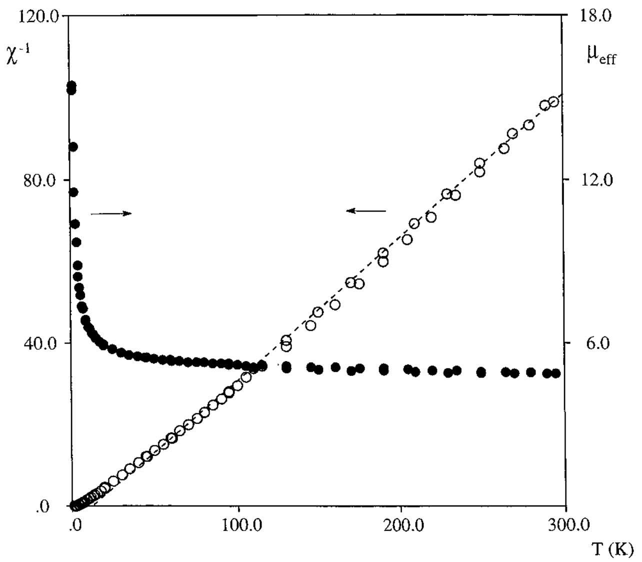


Figure 3. Plots of the effective magnetic moment (●) and the inverse of the magnetic susceptibility (○) for **3** per MnFe vs temperature.

phase in the crystal lattice. Two $[Et_4N]^+$ cations per unit are positioned among the chains, in which all the intermolecular bond distances are longer than 3.3 Å.

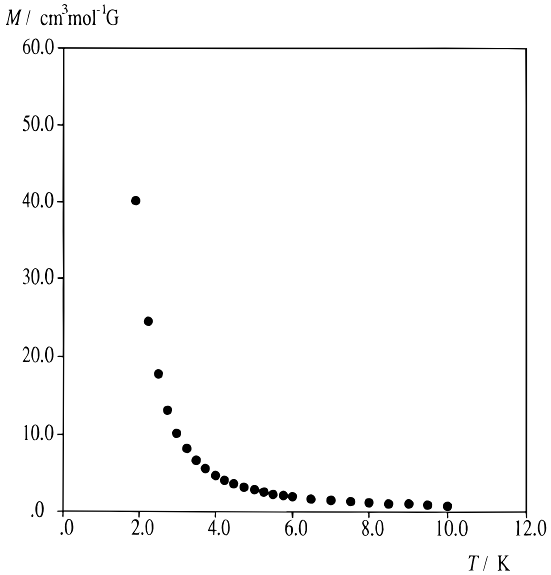


Figure 4. FCM curve (field-cooled magnetization vs T) for **3** under a weak magnetic field of 1 Oe.

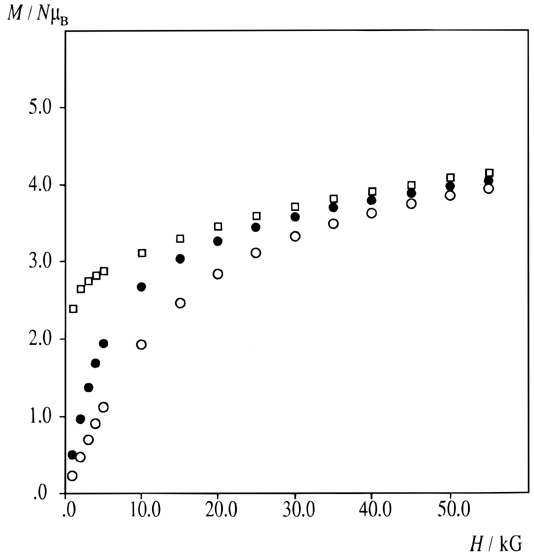


Figure 5. Magnetization as a function of the applied magnetic field up to 55 kOe for **3**, performed at 1.9 K (○), 4.2 K (●), and 6.0 K (□).

Magnetic Properties of 3, a Ferromagnet. The magnetic susceptibility was measured from 1.9 to 300 K by a SQUID magnetometer under the applied magnetic field of 800 G. The plots of μ_{eff} and $1/\chi_M$ vs T are given in Figure 3. The μ_{eff} per MnFe at room temperature, 5.05 μ_B, is slightly lower than the spin-only value of 5.20 μ_B expected for the magnetically dilute two-spin system $(S_{Mn}, S_{Fe}) = (2, {}^1/_2)$, where the spin-only value was calculated by assuming $g_{Mn} = 2.00$ and $g_{Fe} = 2.00$. This is probably due to a low g value for the Mn(III) ion as result of the distorted environment around manganese or/and of a zero-field splitting.[14] It should be noted that slightly low magnetic moments are often found for mononuclear Mn(III) complexes with the acacen ligand.[11] On lowering of the temperature, μ_{eff} first increases gradually and then sharply below 20 K, reaching a value of 15.5 μ_B at 1.9 K. The data above 20 K can be fitted to the Curie–Weiss law with $\Theta = +12.3$ K. The positive value of the Weiss constant along with the absence of a minimum in the μ_{eff} vs T curve indicates a ferromagnetic coupling between iron(III) and manganese(III) ions through a bridging CN group. The value reached by μ_{eff} at 1.9 K is much larger than that of the largest possible spin state $S_T = {}^5/_2$ for the ferromagnetically coupled system $(S_{Mn}, S_{Fe}) = (2, {}^1/_2)$, i.e. 5.92 μ_B, and suggests the onset of a magnetic ordering. The occurrence of a magnetic phase transition was established by measuring the magnetization as function of the temperature under a weak magnetic field. The FCM (field-cooled magnetization) curve was obtained by cooling the sample from 10 to 1.9 K under a magnetic field of 1 Oe and shows a rapid increase below ca. 3 K (Figure 4). At the lowest temperature, 1.9 K, the slope dM/dT of the FCM curve is still increasing so that the critical temperature, taken at the maximum of this slope, is around 1.9 K or probably slightly lower. The field dependence of the magnetization up to 55 kOe was measured at 1.9, 4.5, and 6 K, and the results are shown in Figure 5, where the molar magnetization M is expressed in $N\mu_B$ units (N = Avogadro number) and M is expected to have the saturation value M_s when H/kT becomes very large according to the equation of $M_s = Ng\mu_B S$. The curve at 1.9 K has the behavior expected for a ferromagnet with an extremely large zero-field susceptibility, a very weak magnetic field being sufficient to induce a magnetization of about 3 $N\mu_B$. When the field is increased further, the magnetization increases gradually and is still rising at the highest measured field (55 kOe), indicating that saturation has not yet been reached. The magnetization observed at 55 kOe (4.1 $N\mu_B$) approaches the value $N\mu_B(g_{Mn}S_{Mn} + g_{Fe}S_{Fe}) = 5\ N\mu_B$ expected for a ferromagnet with $g_{Mn} = g_{Fe} = 2.0$. On the other hand, if the coupling were antiferromagnetic, the saturation magnetization would be $N\mu_B(g_{Mn}S_{Mn} - g_{Fe}S_{Fe}) = 3\ N\mu_B$, and as this value is far exceeded, it confirms the ferromagnetic nature of the coupling between Fe(III) and Mn(III) centers along the chain. The magnetization curves taken at temperatures higher than T_c, 4.5 and 6 K, show a gradual increase at low fields with a slope in the limit of zero-field more typical of paramagnetic systems. However, the behavior at higher fields is similar to that observed at 1.9 K, with a gradual increase of the magnetization up to about 4 $N\mu_B$ at 55 kOe. Such a behavior is typical of systems with a relevant anisotropy due to a large zero-field splitting and is consistent with the high values (up to several cm^{-1}) observed for Mn(III) ions in analogous Schiff base compounds.[14] Indeed, even for an isolated spin multiplet, the presence of a zero-field splitting causes the magnetization to increase more slowly than forecast by the corresponding Brillouin function and to reach saturation at much higher fields.

Concluding Remarks. To the best of our knowledge, only three types of one-dimensional compounds exhibiting spontaneous magnetic ordering have been fully characterized from both structural and magnetic viewpoints,[15−17] although several magnetic one-dimensional compounds exhibiting three-dimensional antiferromagnetic ordering have been known.[18,19] These are as follows: (1) A one-dimensional charge-transfer ferromagnetic complex $[Fe(\eta^5\text{-}C_5Me_5)_2]^+[TCNE]^-$ [TCNE = tetracyanoethylene] by was reported Miller and Epstein,[15] in which the $^1/_2$ spins associated with both donor and acceptor units have strong intrachain and weak interchain couplings, thus giving a ferromagnet with $T_c = 4.8$ K. (2) A one-dimensional ferromagnetic oximato-bridged Mn(II)−Cu(II) complex was reported by Kahn and co-workers.[16] The Mn(II) [$S = {}^5/_2$] and Cu(II) [$S = {}^1/_2$] ions display an intrachain antiferromagnetic coupling occurring *via* the intermediacy of the oximato group. The half repeating unit displacement of one chain with regard to the adjacent one gives rise to an overall ferrimagnet. (3) A one-dimensional ferrimagnet Mn(II) hexafluoroacetylacetonato radical complex has been reported by Gatteschi and co-workers.[17] The interchain ferromagnetic coupling, due to the dipolar effect, gives rise to a ferrimagnetic material.

In compound **3** we observed an intrachain ferromagnetic coupling between the high-spin Mn(III) and the low-spin Fe(III) *via* the bridging cyanide anions, while the chains weakly couple to each other ferromagnetically. The result of such couplings is novel and is a rather rare example of a one-dimensional ferromagnet.

This report shows one significant example of the versatility of $[Mn(III)-SB]^+$ and $[Fe(CN)_6]^{3-}$ to assemble a variety of extended structures with relevant magnetic properties, some of which were reported by us recently. They are a two-dimensional network with metamagnetic and a two dimensional network with ferromagnetic properties.[3a,b]

Acknowledgment. This work was supported by the Ministry of Education, Science and Culture of Japan. The Fondation Herbette (University of Lausanne, N.R.) and the Fonds National Suisse de la Recherche Scientifique (Bern, Switzerland; Grant No. 20-40268.94) are also acknowledged for financial support.

Supporting Information Available: Further textural and tabular details of the structure determination and listings of atomic coordinates, anisotropic displacement parameters, bond lengths, bond angles, and nonbonded contacts for complex **3** (19 pages). Ordering information is given on any current masthead page.

IC960556G

---

(14) (a) Boucher, L. J.; Coe, C. G. *Inorg. Chem.* **1975**, *14*, 1289. (b) Bertoncello, K.; Fallon, G. D.; Murray, K. S.; Tiekink, R. T. *Inorg. Chem.* **1991**, *30*, 3562. (c) Chandra, S. K.; Chakraborty, P.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1993**, 863. (d) Bonadies, J. A.; Kirk, M. L.; Lah, M. S.; Kessissoglou, D. P.; Hatfield, W. E.; Pecoraro, V. L. *Inorg. Chem.* **1989**, *28*, 2037. (e) Kennedy, B. J.; Murray, K. S. *Inorg. Chem.* **1985**, *24*, 1552.

(15) Miller, J. S.; Calabrese, J. C.; Rommelmann, H. R.; Chittipeddi, S. R.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769.

(16) Kahn, O.; Pei, Y.; Verdaguer, M.; Renard, J. P.; Sletten, J. *J. Am. Chem. Soc.* **1988**, *110*, 782.

(17) Caneschi, A.; Gatteschi, D.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1989**, *28*, 1976, 3314.

(18) (a) Verdaguer, M.; Gleizes, A.; Renard, J. P.; Seiden, J. *Phys. Rev.* **1984**, *B29*, 5144. (b) Gleizes, A.; Verdaguer, M. *J. Am. Chem. Soc.* **1984**, *106*, 3727. (c) Pei, Y.; Verdaguer, M.; Kahn, O.; Sletten, J.; Renard, J. P. *Inorg. Chem.* **1987**, *26*, 138. (d) Coronado, E.; Drillon, M.; Fuertes, A.; Beltran, D.; Mosset, A.; Galy, J. *J. Am. Chem. Soc.* **1986**, *108*, 900. (e) Coronado, E.; Drillon, M.; Nugteren, P. R.; Jongh, L. J.; Beltran, D.; Georges, R. *J. Am. Chem. Soc.* **1989**, *111*, 3874.

(19) (a) Carlin, R. L. *Magnetochemistry*; Springer: New York, 1986. (b) De Fotis, G. C.; Wiese, R. S.; Scherrer, C. W. *J. Appl. Phys.* **1990**, *67*, 5857.