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Synthesis, Crystal and Network Structures, and Magnetic Properties of a Hybrid Layered Compound: [K(18-cr)(2-PrOH)$_2$][{Mn(acacen)}$_2${Fe(CN)$_6$}] (18-cr = 18-Crown-6-ether, acacen = *N*,*N*′-Ethylenebis(acetylacetonylideneiminate))

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A hybrid layered compound [{K(18-cr)(2-PrOH)$_2$}{Mn(acacen)}$_2${Fe(CN)$_6$}] has been prepared by the reaction of [Mn(acacen)(Cl)] with [K(18-cr)(H$_2$O)$_2$]$_3$[Fe(CN)$_6$]·3H$_2$O in an ethanol/2-propanol mixed solvent (18-cr = 18-crown-6-ether, acacen = *N*,*N*′-ethylenebis(acetylacetonylideneiminate)). It crystallizes in the monoclinic space group $P2_1/a$ with cell dimensions of $a = 13.272(3)$ Å, $b = 15.768$ (2) Å, $c = 14.771(2)$ Å, $\beta = 105.64(1)°$, $Z = 2$. It assumes a hybrid layered structure of alternating arrays of two types of layers. One of the layers is formed by the anionic part [{Mn(acacen)}$_2${Fe(CN)$_6$}]$_n{}^{n-}$, where [Fe(CN)$_6$]$^{3-}$ coordinates through its four cyanide groups on a plane to the axial sites of four [Mn(acacen)]$^+$ entities. The two-dimensional layer consists of the cyclic octamer [−Mn−NC−Fe−CN−]$_4$ having the Fe ions at the corners and the Mn ions on the edges of a deformed square. Another layer is formed by the cationic part [K(18-cr)(2-PrOH)$_2$]$^+$ that has a hexagonal-bipyramidal geometry about the metal with two 2-PrOH molecules at the apexes of the nearly planar [K(18-cr)]$^+$. The anionic and cationic layers are combined by the hydrogen bond between the cyanide groups (free from coordination) of the anionic layer and the 2-propanol groups of the cationic layer with bond distance of N···O = 2.861(5) Å. Magnetic studies (magnetic susceptibility vs *T*, field-cooled magnetization vs *T*, saturation magnetization vs *H*) indicate that the compound is a metamagnet with a Néel temperature $T_N = 5.0$ K, showing the onset of ferromagnetic ordering within the anionic layer and an antiferromagnetic interlayer interaction. Magnetization as a function of the applied magnetic field indicates a spin-flipping from antiferromagnetic arrangement to ferromagnetic arrangement between the layers around 1200 Oe and exhibits hysteresis behavior.

Introduction

Crystal engineering for ordered compounds using metal complexes as the constituents is one of the current subjects aimed toward developing new molecular-based materials.[1] So far most ordered compounds are limited to those of one- or two-dimensional networks,[1−5] and three-dimensional ordered compounds in the true sense are very few.[6] Thus, one crucial step for obtaining functional materials based on one- or two-dimensional networks is how to modulate the interchain or interlayer interaction so as to achieve a novel character from a pseudo-three-dimensional ordering of the constituents. One promising way for providing ordered compounds based on layered constituents is a alternate two types of layers. Such hybrid layered compounds are of great value in developing a "second generation" of molecular-based materials. Intercalated compounds can be regarded as examples of hybrid layered compounds, but molecularly designed systems with a hybrid layered structure are very few.[7]

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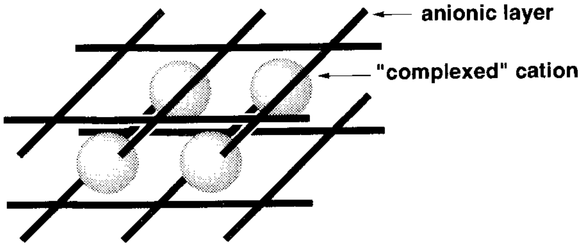
Chart 1



Miyasaka has recently reported on $[A\{Mn(SB)\}_2\{Fe(CN)_6\}]_\infty$ (A = univalent cation, SB = quadridentate Schiff base ligand) compounds derived from the reaction of the constituent complexes $[Mn(SB)(H_2O)]^+$ and $A_3[Fe(CN)_6]$.[8] The compounds consist of anionic two-dimensional layers made from $[\{Mn(SB)\}_2\{Fe(CN)_6\}]^-$ units; the univalent cation is located between the anionic layers. This has prompted us to replace the univalent cation of the compounds by a “complexed” cation in order to obtain hybrid layered compounds compossed of an anionic and a cationic layer (Chart 1).

In this attempt, we chose the potassium ion encapsulated in 18-crown-6-ether, $[K(18\text{-}cr)]^+$ as the complexed cation in this study. A precursor complex $[K(18\text{-}cr)(H_2O)_2]_3[Fe(CN)_6]\cdot 3H_2O$ was prepared and reacted with [Mn(acacen)(Cl)] (acacen = *N*,*N*′-ethylenebis(acetylacetonylideneiminate)) to obtain the hybrid two-dimensional layered compound $[\{K(18\text{-}cr)(2\text{-}PrOH)_2\}\{Mn(acacen)\}_2\{Fe(CN)_6\}]$. The crystal and network structures and the magnetic properties of the compound are reported.

Experimental Section

Physical Measurements. Elemental analyses for C, H, and N were performed at the Elemental Analysis Service Center of Kyushu University. Infrared spectra were measured on KBr disks with JASCO IR-810 and Shimadzu FTIR-8600 spectrophotometers. Preliminary magnetic measurements were made with a Faraday balance over the 80−300 K temperature range, where calibrations were made with $[Ni(en)_3]S_2O_3$ (en = ethylenediamine).[9] Magnetic susceptibilities were finally measured over the 1.8−280 K temperature range using an MPMS5 SQUID susceptometer (Quantum Design, Inc.), where the applied magnetic fields were 10−5000 G. Field dependencies of magnetization up to 5.5 T were studied on the same susceptometer. Corrections were applied for diamagnetism using Pascal’s constants.[10] Effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.828(\chi_M T)^{1/2}$, where χ_M is the magnetic susceptibility per formula unit.

Table 1. Crystallographic Data for $[K(18\text{-}cr)(2\text{-}PrOH)_2][Mn(acacen)]_2[Fe(CN)_6]$

empirical formula	$C_{42}H_{64}N_{10}O_{12}KMn_2Fe$	α/deg	90
fw	1105.85	β/deg	105.64(1)
crystal system	monoclinic	γ/deg	90
space group	$P2_1/a$ (#14)	V/Å^3	2976.7(9)
T/°C	23 ± 1	Z	2
λ/Å	0.71069	D_{cal}/g cm^{-3}	1.234
a/Å	13.272(3)	μ(Mo Kα)/cm^{-1}	7.85
b/Å	15.768(2)	no. of reflections	7401
c/Å	14.771(2)	R^a	5.6
		$R_w^{b,c}$	5.5

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

X-ray Data Collection, Reduction, and Structure Determination. Single crystals were prepared by the method described in the synthetic procedure. A single crystal for the crystallographic analysis was cut from a thin plate crystal and mounted on a glass rod. The crystal dimensions were 0.35 × 0.40 × 0.45 mm. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation (λ = 0.710 69 Å) and a 12 kW rotating anode generator. The data were collected at a temperature of 23 ± 1 °C using $\omega-2\theta$ scan technique to a maximum 2θ value of 55.0° at a scan speed of 16.0°/min (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 4 scans), and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. Of the 7401 reflections which were collected, 7104 were unique. The diameter of the incident beam collimator was 1.0 mm, the crystal-to-detector distance was 235 mm, and the computer-controlled detector aperture was set to 9.0 × 13.0 mm (horizontal vertical). 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 corrections were applied by a polynomial correction. An empirical absorption correction based on azimuthal scans of several reflections was applied. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods[11] and expanded using Fourier techniques.[12] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. Full-matrix least-squares refinements based on 5291 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. The weighting scheme was based on counting statistics. Plots of $\Sigma w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. Neutral atomic scattering factors were taken from Cromer and Waber.[13] Anomalous dispersion effects were included in F_{calcd}; the values $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[14] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[15] All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.[16] The crystal data and details of the structure determinations are summarized in Table 1.

General Procedures and Materials. All chemicals and solvents used for the synthesis were reagent grade. The H_2acacen was synthesized by mixing acetylacetone and ethylenediamine in a 2:1 molar ratio according to the literature.[17] [Mn(acacen)(Cl)] was prepared by the anion replacement reaction of [Mn(acacen)(OAc)] in a water/

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chloroform mixture according to the method previously reported.[18] Because hexacyanoferrate(III) ion has a tendency to decompose on heating and irradiation, the syntheses of the $Mn^{III}-Fe^{III}$ assembly compound were carried out at room temperature and the crystallization was performed in the dark.

Preparation of the Precursor Complex $[K(18\text{-}cr)(H_2O)_2]_3[Fe(CN)_6]\cdot 3H_2O$. To a suspension of $K_3[Fe(CN)_6]$ (3.29 g, 10 mmol) in 80 cm^3 of methanol was added a solution of 18-crown-6-ether (7.93 g, 30 mmol) in 100 cm^3 of methanol at room temperature under anaerobic conditions. The orange-yellow suspension was stirred at room temperature for 6 h in a dark room, and the resulting yellow solution was filtered and concentrated to 30 cm^3 by a vacuum-evaporation apparatus below 50 °C. The yellow solid that deposited was triturated with diethyl ether, separated and dried in vacuo. Anal. Calcd for $C_{42}H_{90}N_6O_{27}K_3Fe$: C, 39.28; H, 7.06; N, 6.54. Found: C, 39.28; H, 7.03; N, 6.59. IR (KBr): $\nu_{C\equiv N}$(cyanide), 2110 cm^{-1}.

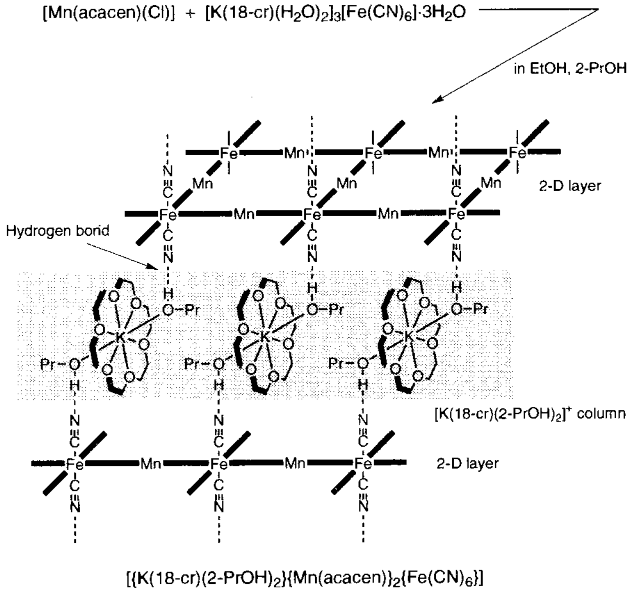
Preparation of $[\{K(18\text{-}cr)(2\text{-}PrOH)_2\}\{Mn(acacen)\}_2\{Fe(CN)_6\}]$. To a solution of [Mn(acacen)(Cl)] (156 mg, 0.5 mmol) in 20 cm^3 of ethanol was added a solution of $[K(18\text{-}cr)(H_2O)_2]_3[Fe(CN)_6]\cdot 3H_2O$ (642 mg, 0.5 mmol) in 10 cm^3 of ethanol, and the resulting solution was filtered to separate any insoluble materials. The dark brown filtrate was diluted with 30 cm^3 of 2-propanol and allowed to stand for 2−3 days in a dark room to form $[\{K(18\text{-}cr)(2\text{-}PrOH)_2\}\{Mn(acacen)\}_2\{Fe(CN)_6\}]$ as dark brown crystals suitable for X-ray crystallography. They were collected by suction filtration, washed with a minimum amount of 2-propanol and dried in vacuo. Anal. Calcd for $C_{48}H_{76}N_{10}O_{12}K_1Mn_2Fe$: C, 48.45; H, 6.44; N, 11.77. Found: C, 48.07; H, 6.34; N, 11.77. IR(KBr): $\nu_{C=N}$(imine), 1583 (broad) cm^{-1}; $\nu_{C\equiv N}$(cyanide), 2068 and 2102 cm^{-1}.

Results and Discussion

Synthesis. To provide hybrid layered compounds, it is necessary to prepare a building component for the second layer in one of the building blocks for the first layer. In this study, $[K(18\text{-crown-6-ether})]^+$ was chosen as the component for the second layer and $[K(18\text{-}cr)(H_2O)_2]_3[Fe(CN)_6]\cdot 3H_2O$ was prepared as a precursor complex. It was prepared by reaction of $K_3[Fe(CN)_6]$ and 18-crown-6-ether (1:3 in molar ratio) in methanol. The precursor complex is soluble in most polar organic solvents. This enabled us to use it for preparing hybrid layered compounds by reaction in nonaqueous media. The hybrid compound $[\{K(18\text{-}cr)(2\text{-}PrOH)_2\}\{Mn(acacen)\}_2\{Fe(CN)_6\}]$ was obtained by reaction of $[K(18\text{-}cr)(H_2O)_2]_3[Fe(CN)_6]\cdot 3H_2O$ with [Mn(acacen)(Cl)] in an ethanol/2-propanol mixed solvent, as shown in Scheme 1. Single crystals suitable for X-ray crystallography were obtained in ca. 30% yield, when the reaction mixture was allowed to stand for 3 days. Prolonged standing of the reaction mixture resulted in contamination by the precursor complex.

Structural Study of Hybrid Layered Compound. Perspective views of the anionic part, $[\{Mn(acacen)\}_2\{Fe(CN)_6\}]^-$, and the cationic part, $[K(18\text{-}cr)(2\text{-}PrOH)_2]^+$, are given in Figure 1, together with the numbering scheme of the unique atoms. The relevant bond distances and angles are summarized in Table 2. Figure 2 shows the two-dimensional network structure consisting of a cyclic octamer [−Mn−NC−Fe−CN−]$_4$ as a net unit which is the view projected along the *c* axis. Figure 3 shows the hybrid two-dimensional layered structure composed of anionic and cationic layers, where the figure on the left is the view projected onto the *bc* plane and that on right is the view projected onto the *ac* plane.

Scheme 1



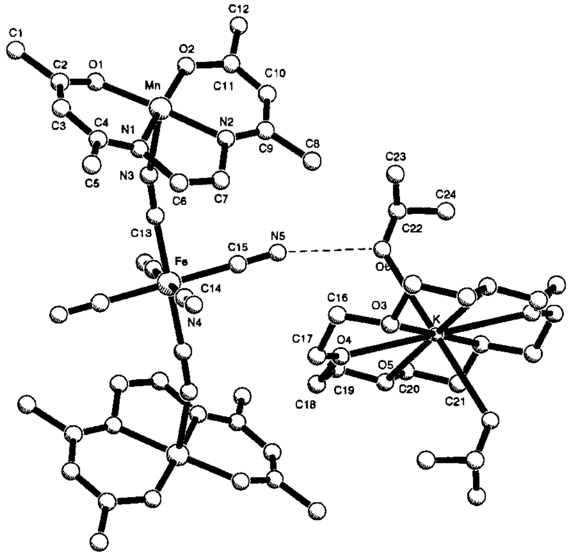


Figure 1. Perspective view of $[K(18\text{-}cr)(2\text{-}PrOH)_2][Mn(acacen)]_2[Fe(CN)_6]$ moiety with the atom numbering scheme of the unique atoms.

The $[Fe(CN)_6]^{3-}$ coordinates through its four cyano nitrogens on a plane to the axial site of the four $[Mn(acacen)]^+$ entities, providing a two-dimensional network as shown in Figure 2. The 2-D network consists of cyclic octamer [−Mn−NC−Fe−CN−]$_4$ units having the Fe ions at the corners and the Mn ions on the edges of a deformed square, where Fe ions occupy the inversion centers ($^1/_2$, 0, $^1/_2$). This is clearly seen in a projection onto the *ab* plane (Figure 2). The Fe−C(13), N(3)−Mn, and C(13)−N(3) bond distances in the trinuclear unit, [Mn−NC−Fe−CN−Mn], are 1.947(3), 2.331(3), and 1.153(4) Å, respectively, and the Fe−C(13)−N(3) and C(13)−N(3)−Mn angles are 176.8(3) and 152.0(3)°, respectively. Two more CN^- groups of $[Fe(CN)_6]^{3-}$ in the trinuclear unit are bound to the Mn ions of the adjacent trinuclear units with the dimensions of Fe−C(14) = 1.954(3) Å, Mn*−N(4) = 2.439(3) Å, C(14)−N(4) = 1.143(4) Å, Fe−C(14)−N(4) = 178.4(3)°, C(14)−N(4)−Mn* = 154.8(3)°. The deformation of the square unit evidently arises from the small C−N−Mn angle. The remaining cyanide groups, free from coordination, have Fe−C bond distances comparable to those involved in the bridge to the Mn ions (Fe−C(15) = 1.955(3) Å). Thus, the geometry about Fe is nearly octahedral.

The geometry about Mn is an elongated octahedron. This is due to the Jahn−Teller effect of the high-spin d^4 electronic configuration of Mn(III) and also the strong in-plane donation

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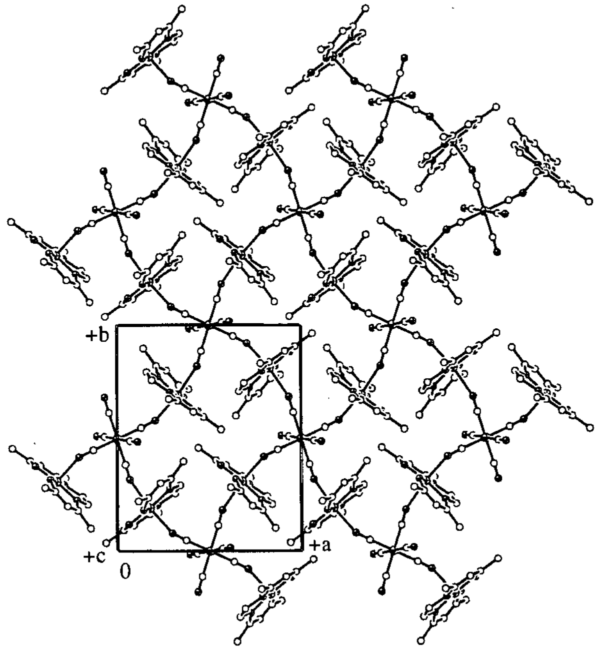

Figure 2. Projection of the anionic layer along the *c*-axis of [K(18-cr)(2-PrOH)$_2$][Mn(acacen)]$_2$[Fe(CN)$_6$], showing a two-dimensional network structure consisting of cyclic octamer unit [−Mn−NC−Fe−CN−]$_4$.

Table 2. Relevant Bond Distances (Å) and Angles (deg) for [K(18-cr)(2-PrOH)$_2$][Mn(acacen)]$_2$[Fe(CN)$_6$] with the Estimated Standard Deviations in Parentheses[a]

Bond Distances (Å)			
Mn−N1	1.944(4)	Mn−N2	1.968(5)
Mn−N3	2.331(3)	Mn−N4*	2.439(3)
Mn−O1	1.888(3)	Mn−O2	1.892(3)
Fe−C13	1.947(3)	Fe−C14	1.954(3)
Fe−C15	1.955(3)	C13−N3	1.153(4)
C14−N4	1.143(4)	C15−N5	1.151(4)
K−O3	2.877(4)	K−O4	2.672(3)
K−O5	2.792(4)	K−O6	2.794(4)
Bond Angles (deg)			
N1−Mn−N3	92.0(1)	N1−Mn−N4*	81.1(1)
N2−Mn−N3	84.5(1)	N2−Mn−N4*	91.4(2)
N3−Mn−N4*	172.3(1)	O1−Mn−N3	95.0(1)
O1−Mn−N4*	88.8(1)	O2−Mn−N3	93.7(1)
O2−Mn−N4*	93.0(1)	C13−Fe−C14	88.5(1)
C13−Fe−C15	88.0(1)	C14−Fe−C15	88.7(1)
Mn−N3−C13	152.0(3)	Mn−N4*−C14*	154.8(3)
Fe−C13−N3	176.8(3)	Fe−C14−N4	178.4(3)
Fe−C15−N5	177.7(3)		
Hydrogen Bond Distances (Å)			
O6···N5	2.861(5)		

[a] Symmetry operation (*): $^1/_2 + x$, $^1/_2 - y$, z.

of the acacen^{2-} ligand. The in-plane Mn-to-ligand bond distances fall in the 1.888(3)−1.968(5) Å range, whereas the axial Mn−N bond distances are elongated (Mn−N(3) = 2.331(3) and Mn−N(4)* = 2.439(3) Å).

The cationic part [K(18-cr)(2-PrOH)$_2$]$^+$ has a hexagonal-bipyramidal geometry about the potassium ion. The [K(18-cr)]$^+$ entity forms a mean molecular plane by six ether oxygens (O3, O4, O5, O3*, O4*, O5*), and the two 2-PrOH molecules occupy the apexes; the potassium resides at the inversion center ($^1/_2$, 0, 0). The basal K−O distances (K−O3, K−O3*, K−O4, K−O4*, K−O5, K−O5*) and the axial distances (K−O6, K−O6*) are similar and fall in the 2.672(3)−2.877(4) Å range. The [K(18-cr)(2-PrOH)$_2$]$^+$ cations arrange along the *a* axis, with the [K(18-cr)]$^+$ mean plane almost perpendicular to the axis, forming a one-dimensional column running along the axis. Further more, the one-dimensional columns are aligned along the *b* axis so as to provide a pseudo-two-dimensional sheet extended onto the *bc* plane (see Figure 3).

Thus, the bulk structure of the compound consists of the alternating array of the two-dimensional network of the anionic component and the pseudo-two-dimensional network of the cationic component. The two layers are connected through hydrogen bonds between the two cyanide nitrogens (free from bridging) of the anionic layer and the 2-PrOH hydrogens in the cationic layer with a bond distance of N(5)···O(6) = 2.861(5) Å. The nearest interlayer Fe···K and Mn···K separations are 7.39 and 8.14 Å, respectively. The nearest interlayer (between the anionic layers) Fe···Fe (Mn···Mn), Fe···Mn separations are 14.80 and 14.63 Å, respectively.

Magnetic Properties of Hybrid Layered Compound. The magnetic susceptibility of the hybrid compound was measured from 1.8 to 280 K on a SQUID magnetometer under an applied magnetic field of 5000 Oe. The $\mu_{\rm eff}$ vs T and $1/\chi_{\rm M}$ vs T curves are shown in Figure 4. The effective magnetic moment per [Mn$_2$Fe] at room temperature is 7.76 $\mu_{\rm B}$, which is slightly larger than the spin-only value, 7.14 $\mu_{\rm B}$, for the magnetically dilute three-spin system ($S_{\rm Mn}$, $S_{\rm Fe}$, $S_{\rm Mn}$) = (2, $^1/_2$, 2), the spin-only value being calculated by assuming $g_{\rm Mn} = 2.00$ and $g_{\rm Fe} = 2.00$. The plot of $1/\chi_{\rm M}$ vs T above 30 K obeys the Curie−Weiss law with a positive Weiss constant of $\theta = +2.3$ K. As the temperature is lowered, $\mu_{\rm eff}$ increases first gradually and then sharply below 20 K up to a maximum value of 10.92 $\mu_{\rm B}$ at 5 K and finally sharply decreases to 7.88 $\mu_{\rm B}$ at 1.8 K. The positive Weiss constant suggests a ferromagnetic interaction between the high-spin Mn(III) ion of [Mn(acacen)]$^+$ and the low-spin Fe(III) ion of [Fe(CN)$_6$]$^{3-}$ via the bridging CN$^-$ group. The ferromagnetic interaction operating between high-spin Mn(III) and low-spin Fe(III) is not surprising. In fact, both ferromagnetic and antiferromagnetic interactions have been observed for related compounds with Fe$^{\rm III}$-CN−Mn$^{\rm III}$ linkage.[8a,b,20] Assuming Oh symmetry for Fe(III) and an axially elongated Oh symmetry for Mn(III), Fe(III) has the electronic $(t_{2g})^1$ ($t_{2g} = d_{xy}, d_{yz}, d_{zx}$) configuration and Mn(III) has the electronic $(d_{xy})^1(d_{yz})^1(d_{zx})^1(d_{z^2})^1$ configuration. The magnetic interaction between the spin of Fe(III) and the spin in the d_{z^2} orbital of Mn(III) is ferromagnetic due to the "strict orthogonality" of magnetic orbitals.[19] Antiferromagnetic interaction may occur when the spin on the t_{2g} orbital of Fe(III) and the spins on the orbitals d_{xy}, d_{yz}, and d_{zx} of the Mn(III) are effectively exchanged by a π pathway. In the case of the present compound, the antiferromagnetic contribution through the π mechanism must be small because (1) the axial N−Mn bond is significantly elongated and (2) the Fe−C−N−Mn linkage is largely bent at the nitrogen. In agreement with this consideration, a related one-dimensional compound [NEt$_4$]$_2$[{Mn(acacen)}{Fe(CN)$_6$}][20] has a long Mn−N distance (2.316(4) Å) and a largely bent Mn−N−C angle (152.6(3)°) in the Mn−NC−Fe linkage and shows ferromagnetic interaction between Mn(III) and Fe(III) through a cyanide bridge.

The maximum value of $\mu_{\rm eff}$ at 5 K is larger than 9.95 $\mu_{\rm B}$ for the possible total spin state $S_{\rm T} = {}^9/_2$ arising from ferromagnetic coupling in the [{Mn(acacen)}$_2${Fe(CN)$_6$}]$^-$ unit ($S_{\rm Mn}$, $S_{\rm Fe}$, $S_{\rm Mn}$) = (2, $^1/_2$, 2), indicating that an intralayer ferromagnetic ordering is obtained.

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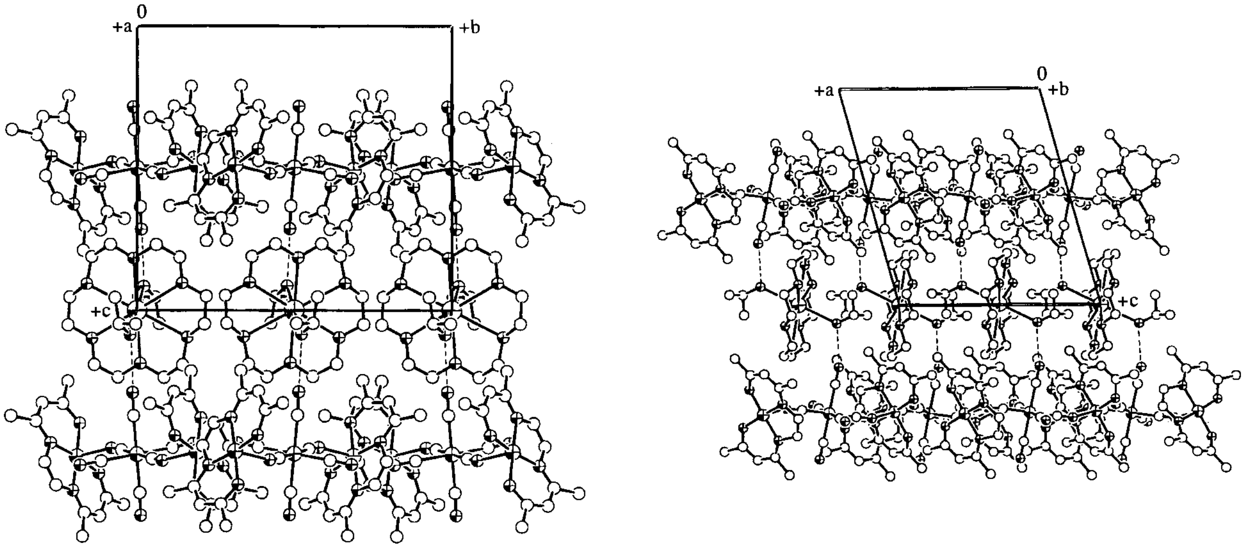

Figure 3. Projections of hybrid layered structure onto the *bc* plane (left) and the *ac* plane (right).

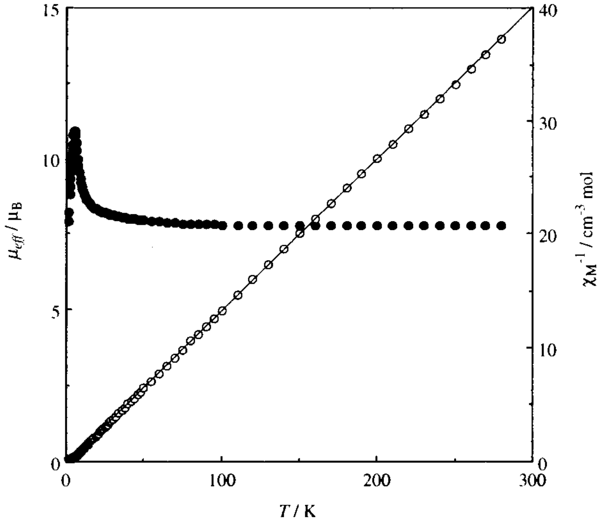

Figure 4. Plots of $\mu_{\rm eff}$ (●) and $1/\chi_{\rm M}$ (○) vs *T* for [K(18-cr)(2-PrOH)$_2$][Mn(acacen)]$_2$[Fe(CN)$_6$] per [Mn$_2$Fe].

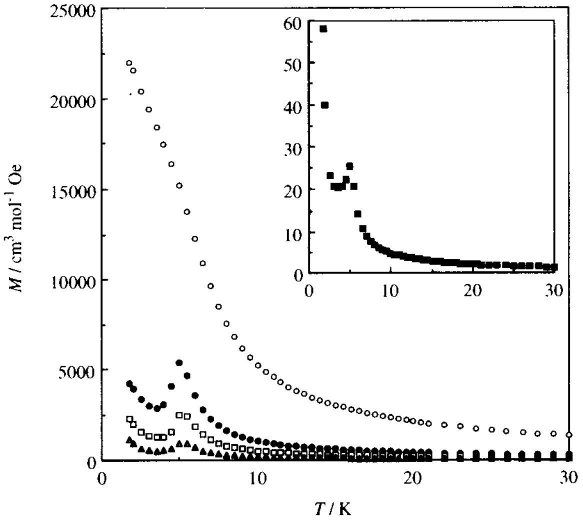

Figure 5. FCM (field-cooled magnetization) vs *T* curves under several magnetic fields; 10 (■), 200 (△), 500 (□), 1000 (●), and 5000 (○) Oe.

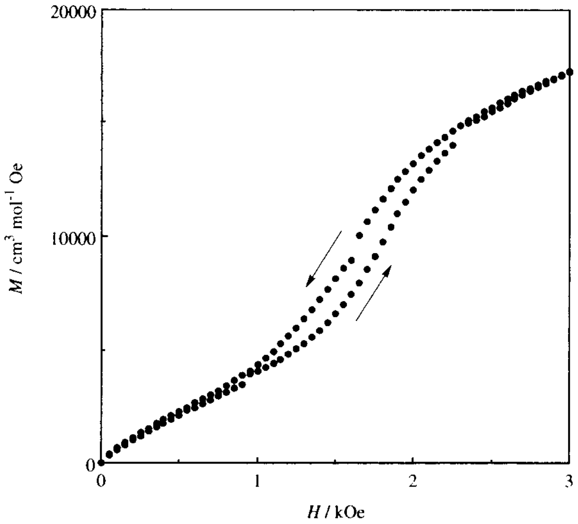

Figure 6. Magnetization as the function of external magnetic field at 1.8 K. Arrows show the increase and decrease processes of applied magnetic fields.

FCM (field-cooled magnetization vs *T*) data were measured by cooling a powdered sample of the compound from 30 to 1.8 K under different magnetic fields (10, 200, 500, 1000, and 5000 Oe). The results are shown in Figure 5. The FCM curves obtained at 10, 200, 500, and 1000 Oe show a sharp peak at 5.0 K (Néel temperature), but the FCM curve obtained at 5000 Oe shows no such peak. This magnetic behavior is typical of a metamagnet. To further confirm the metamagnetic transition in this compound, the magnetization was measured as a function of the external magnetic field at temperatures above and below the Néel temperature (5.0 K). The result obtained at 1.8 K is shown in Figure 6, which evidences a spin-flipping from antiferromagnetic to ferromagnetic spin arrangement around 1200 Oe. It is noteworthy that the magnetic field causing the spin-flipping depends on the upward or downward field variation, exhibiting hysteresis of the spin-flipping phenomenon. Figure 7a shows the magnetization behavior in an applied magnetic field up to 10 kOe at 1.8 and 5.5 K. The magnetization smoothly increases with the applied magnetic field when measured at 5.5 K but shows a break around 1200 Oe for a faster increase when measured at 1.8 K. This fact suggests that the intralayer ferromagnetic ordering is incomplete at 5.5 K, but is reached at 1.8 K, further supporting the metamagnetic nature of the hybrid layered compound with an interlayer antiferromagnetic interaction.

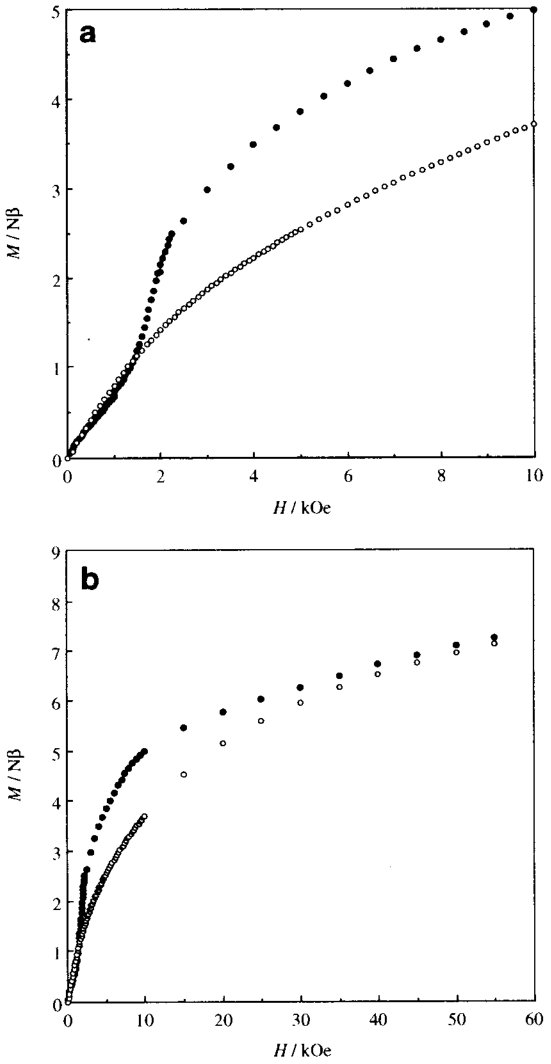

Figure 7. (a) Field-dependence of magnetization over the field range of 0−10 kOe and (b) up to 55 kOe, determined at 1.8 K (●) and 5.5 K (○).

Figure 7b clearly indicates that the magnetization is not saturated even at 55 kOe: the magnetization value of ca. 7 Nβ at 55 kOe is smaller than the 9 Nβ expected for the ferromagnetically coupled (S_{Mn}, S_{Fe}, S_{Mn}) = (2, $^1/_2$, 2) system based on the equation Ms = $N\beta(2g_{Mn}S_{Mn} + g_{Fe}S_{Fe})$. Such a slow saturation of the magnetization can be ascribed to a large zero-field splitting of the Mn(III) ion;[8b] a splitting of several wavenumbers has been found for the Mn(III) complexes of acacen^{2-}, salen^{2-} (*N*,*N′*-ethylenebis(salicylideneiminate)), and related Schiff base ligands.[21]

It is of interest to compare the interlayer magnetic interaction of the hybrid layered compound with a related compound K[Mn-(3-MeOsalen)]$_2$[Fe(CN)$_6$]·2DMF[8a,b] that has a similar two-dimensional network structure consisting of the octamer net unit [−Mn−NC−Fe−CN−]$_4$ and exhibits a metamagnetic nature. The interlayer separation of this compound (13.1 Å) is smaller than in the hybrid layered compound (14.8 Å). The applied magnetic field required for the spin-flipping is 200 Oe for the former, whereas it is 1200 Oe for the latter. Therefore, the spin-flipping field does not seem to be correlated to the interlayer separation. It is interesting to point out that the hybrid layered compound has a hydrogen-bonded network that may contribute to interlayer magnetic interactions.

Concluding Remarks

A promising method for providing hybrid layered compounds is described. The reaction of [Mn(acacen)(Cl)] with [K(18-cr)(H$_2$O)$_2$]$_3$[Fe(CN)$_6$]·3H$_2$O in an ethanol/2-propanol mixture solvent gave [K(18-cr)(2-PrOH)$_2$][Mn(acacen)]$_2$[Fe(CN)$_6$], which consists of an alternating array of anionic and cationic layers. The anionic layer formed by [{Mn(acacen)}$_2${Fe(CN)$_6$}]$^-$ consists of a cyclic octamer unit [−Mn−NC−Fe−CN−]$_4$ having Fe ions at the corners and Mn ions at the edges of a deformed square. The cationic layer is formed by a two-dimensional arrangement of [K(18-cr)(2-PrOH)$_2$]$^+$. The two layers are connected through hydrogen-bonds between the two cyanide nitrogens (free from bridging) of the anionic layer and the 2-PrOH hydrogens in the cationic layer (N(5)···O(6) = 2.861(5) Å). [K(18-cr)(2-PrOH)$_2$][Mn(acacen)]$_2$[Fe(CN)$_6$] exhibits a metamagnetic behavior due to intralayer ferromagnetic interaction and interlayer antiferromagnetic interaction. Despite the large separation between the nearest anionic layers (14.8 Å), the interlayer antiferromagnetic interaction is unexpectedly strong enough to yield spin-flipping at 1200 Oe. It may be due to the hydrogen-bond through the cationic layer.

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Supporting Information Available: The X-ray crystallographic file, in CIF format, is available. Access information is given on any current masthead page.

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