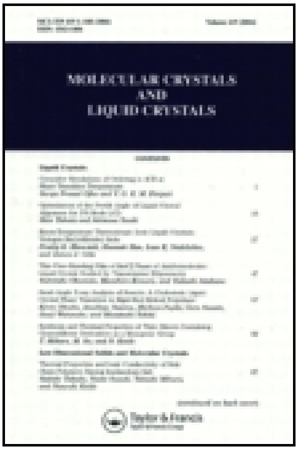

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Ferrimagnetic Property of Two-Dimensional Layered Compound $K[Mn(3\text{-}MeOsalen)]_2[Cr(CN)_6]{\bullet}H_2O$

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A series of bimetallic compounds of the general formula $K[Mn(3\text{-}MeOsalen)]_2[M(CN)_6]$ ($M = Co^{3+}, Fe^{3+}, Mn^{3+}, Cr^{3+}$) has a similar 2-D network structure but their magnetic properties vary depending upon the nature of the metal ion of $[M(CN)_6]^{3-}$ and the interlayer magnetic interaction. The magnetic property of $K[Mn(3\text{-}MeOsalen)]_2[Cr(CN)_6]{\bullet}H_2O$ shows a ferrimagnetic nature arising from an intralayer ferrimagnetic ordering due to the antiferromagnetic spin arrangement of neighboring high spin Mn^{3+} and Cr^{3+}, and an interlayer ferromagnetic interaction.

Keywords: ferrimagnet; two-dimensional layered compound; manganese(III) salen analogous; hexacyanochromate(III)

INTRODUCTION

$K[Mn(3\text{-}MeOsalen)]_2[M(CN)_6]$ ($M = Fe^{3+}$ and Mn^{3+}, 3-MeOsalen = *N*, *N'*-ethylenebis(3-methoxysalicylideneiminato)) has been reported previously to have a two-dimensional network structure consisting of octamer $[\text{-Mn-NC-Fe-CN-}]_4$ net units as shown in Figure 1 and to show a metamagnetic nature.[1-3] The metamagnetism arises from an intralayer ferromagnetic interaction and an interlayer antiferromagnetic interaction. The intralayer ferromagnetic interaction is due to the magnetic interaction between high-spin Mn(III) in the [Mn(3-

MeOsalen)]$^+$ component and low-spin M(III) in the $[M(CN)_6]^{3-}$ component through bridging CN groups (Figure 1). If the building component, $[Fe(CN)_6]^{3-}$, in the two-dimensional network is substituted by $[Cr(CN)_6]^{3-}$, the magnetic behavior of the resulting hetero-metalic assemblies, $K[Mn(3\text{-}MeOsalen)]_2[Cr(CN)_6]$, would reflect the magnetic interaction between the adjacent Mn(III) and Cr(III) ions. From this viewpoint, in this context, the analogous compound of $[Mn_2Fe]$, $K[Mn(3\text{-}MeOsalen)]_2[Cr(CN)_6]$, was prepared and its magnetic properties investigated. The X-ray powder diffraction analyses for this compound and $[Mn_2M]$ ($M = Co^{3+}, Fe^{3+}, Mn^{3+}$) compounds indicate that these compounds are isomorphous.

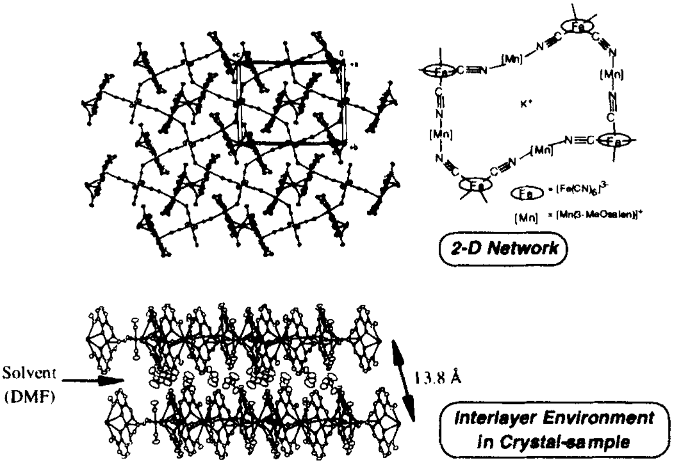


FIGURE 1 Two-dimensional network and interlayer environment of $K[Mn(3\text{-}MeOsalen)]_2[Fe(CN)_6]\cdot 2DMF$.[1,2]

EXPERIMENTAL

Preparation of $K[Mn(3\text{-}MeOsalen)]_2[Cr(CN)_6]\cdot H_2O$

To an ice-cooled solution of $[Mn(3\text{-}MeOsalen)(H_2O)]ClO_4$ (249 mg, 0.5 mmol) in methanol (50 mL) was added an ice-cooled solution of $K_3[Cr(CN)_6]$ (162 mg, 0.5 mmol) in water (5 mL). The resulting solution was allowed to stand for 30 min in an ice-bath to give a reddish brown precipitate, which was collected by suction filtration, washed with 1 : 1 v/v methanol-water and dried *in vacuo*. (yield 95 % (Mn)) Anal. Calcd for $C_{42}H_{38}N_{10}O_9KCrMn_2$: C, 49.08; H, 3.73; N, 13.63; Mn, 10.69; Cr, 5.06. Found; C, 49.43; H, 3.73; N, 13.62; Mn, 10.40; Cr, 4.25. IR(KBr): ν[C=N (imine)] 1601, 1624 cm^{-1}; ν[C≡N (cyanide)] 2114, 2139 cm^{-1}. M.p.: > 300 °C.

X-ray Powder Diffraction Analysis

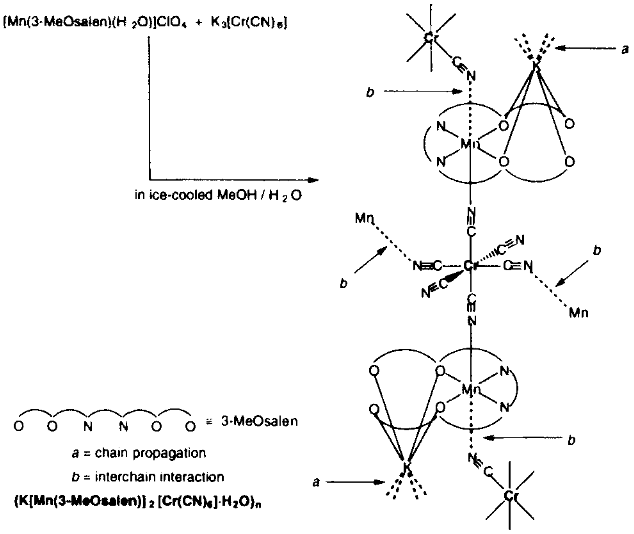
X-ray diffraction patterns of powdered samples were recorded on a RINT-2500 of Rigaku Co. Ltd. model with a graphite monochromator, Cu-Kα radiation (λ = 1.5418 Å) at 50kV and 300 mA. Data were obtained from 2 to 90 ° (2θ) at scan speed of 4 °/min.

RESULTS AND DISCUSSION

General Characterization

The two building components, $[Mn(3\text{-}MeOsalen)(H_2O)]ClO_4$ and $K_3[Cr(CN)_6]$, were reacted in a 1 : 1 molar ratio in methanol/water mixed solution at ice-cooled temperature (see experimental section) to give the 2 : 1 compound $K[Mn(3\text{-}MeOsalen)]_2[Cr(CN)_6]\cdot H_2O$ as shown in Scheme 1.[2] This compound was easily synthesized, however heating of the mixture would let to decompose the $K_3[Cr(CN)_6]$ and give byproducts, so preparation of this compound was carried out in an ice bath. Although the component Mn(III) and Cr(III) compounds were mixed not only in the molar ratio of 1 : 1, but also, in 2 : 1 and 3 : 1 ratios, the resulting products were always in the stoichiometry 2 : 1. These compounds were identified by their microanalyses including Mn and Cr. The component $K_3[Cr(CN)_6]$ showed a single sharp ν(C≡N) band at 2135 cm^{-1}. The ν(C≡N) band of $[Mn_2Cr]$ compound is split into two bands, 2114 and 2139 cm^{-1}. Such a splitting of the ν(C≡N) mode into two was observed for $K[Mn(3\text{-}MeOsalen)]_2[M(CN)_6]$ ($M = Co^{3+}, Fe^{3+}, Mn^{3+}$) having the same 2-D sheet structure; 2106, 2124 cm^{-1} for $M = Co^{3+}$, 2114 and 2097 cm^{-1} for $M = Fe^{3+}$, and 2089 and 2111 cm^{-1} for $M = Mn^{3+}$.

SCHEME 1



Powder X-ray Diffraction Studies

Powder X-ray diffraction studies were carried out with K[Mn(3-MeOsalen)]$_2$[M(CN)$_6$] (M = Co^{3+}, Fe^{3+}, Mn^{3+}) as references in the 2θ range of 2 to 90 ° (in Figure 2, the data measured in the 2θ range of 2 to 40 ° are shown). The results indicate that each pair of [Co-crystal and Fe-crystal], [Co-powder and Fe-powder], and [Mn and Cr] (M-crystal = grained crystal sample and M-powder = powder sample) are very similar in the crystal structure and packing to each other and that the interlayer *d*-spacing decreases slightly in the order [Co-crystal and Fe-crystal]>[Co-powder and Fe-powder]>[Mn and Cr]. Although absorption intensity decreases in the order [Co-crystal and Fe-crystal]>[Co-powder and Fe-powder]>[Mn and Cr], these diffraction patterns are similar to each other. This fact shows that these complexes have the same two-dimensional framework except for the interlayer *d*-spacing and the environment between the two-dimensional sheets (see Figure 1).

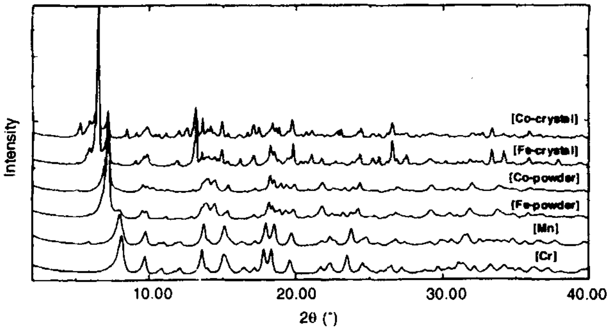


FIGURE 2 Powder X-ray diffraction pattern ($2 < 2\theta < 40$ °).

Magnetic Properties of $K[Mn(3\text{-}MeOsalen)]_2[Cr(CN)_6]\cdot H_2O$

The magnetic susceptibility was measured from 4.2 K to 300 K in an applied magnetic field of 100 Oe. Plots of μ_{eff} vs. T and $1/\chi_M$ vs. T per [Mn_2Cr] are shown in Figure 3. The μ_{eff} at room temperature, 7.60 μ_B, is slightly smaller than the spin-only value of 7.94 μ_B for a magnetically dilute spin-system (S_{Mn} *h. s.*, S_{Cr}, S_{Mn} *h. s.*) = (2, 3/2, 2), where the spin-only value was calculated by assuming $g_{Mn} = 2.00$ and $g_{Cr} = 2.00$. The plots of $1/\chi_M$ vs. T above 30 K obey the Curie-Weiss law with a negative Weiss constant of $\theta = -33.6$ K, indicating antiferromagnetic interactions. On lowering the temperature from room temperature, μ_{eff} decreases gradually showing a minimum of 6.10 μ_B at 30K, then increases gradually, and finally increases abruptly to 16.72 μ_B at 4.4 K. The minimum value of μ_{eff} is close to the spin-only value of $S_T = 5/2$ which is expected for the system of S_{Mn} *h. s.*, S_{Cr}, S_{Mn} *h. s.*) = (2, 3/2, 2). This magnetic behavior demonstrates that the magnetic interaction between Mn and Cr is antiferromagnetic and ferrimagnetic ordering occurs within each layer. No decreasing of the magnetization at critical temperature exhibits that the magnetic interaction between layers is either very weak or ferromagnetic relative to the magnetic ordering within each layer.

To confirm the magnetic transition, FCM (field cooled magnetization), RM (remnant magnetization) and ZFCM (zero-field cooled magnetization) curves vs.

T were measured under zero and 10 Oe magnetic fields as shown in Figure 4. On lowering the temperature, FCM curve at 10 Oe shows a rapid increase below ca. 12 K and a break in the curve around T_c = 11 K. When the field was switched off at 4.4 K, a RM was observed which vanished at T_c upon warming. The ZFCM vs. *T* curve was obtained by cooling the sample in zero field and warming it at 10 Oe. The ZFCM value at 4.4 K is a relatively large value and decreases upon warming, however at ca. 10 K it shows a peak. The abrupt increase of the magnetization indicates the on-set of long range magnetic ordering due to the ferrimagnetic coupling within each layer and below 10 K indicates the presence of interlayer ferromagnetic interactions. As a result, this complex has a spontaneous magnetization, where within each layer the coupling between hetero-metal ions is antiferromagnetic and between layers is ferromagnetic.

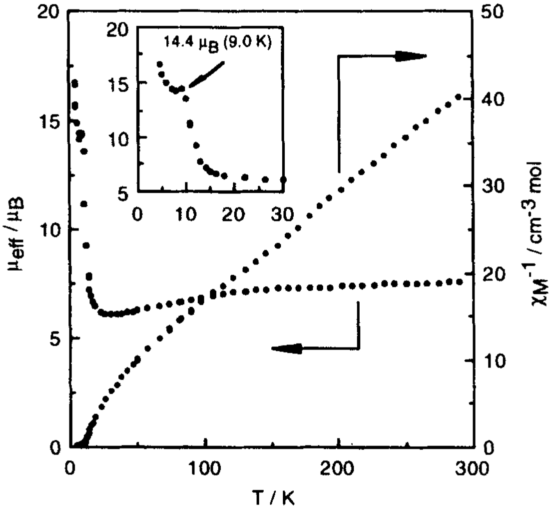


FIGURE 3 Plots of the effective magnetic moment (μ_{eff}) and $1/\chi_M$ for $K[Mn(3\text{-}MeOsalen)]_2[Cr(CN)_6]\cdot H_2O$ per $[Mn_2Cr]$ vs. temperature.

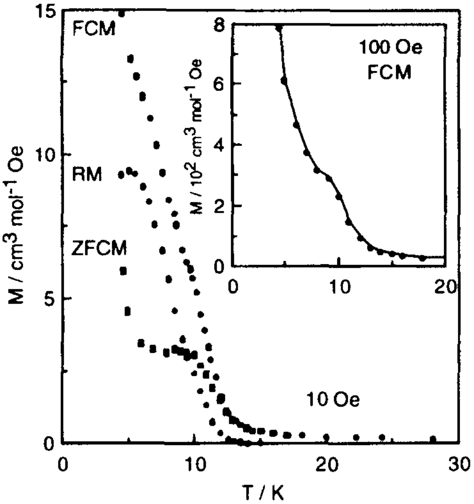


FIGURE 4 FCM (field-cooled magnetization) curve under 10 Oe, RM (remnant magnetization), and ZFCM (zero-field cooled magnetization) for K[Mn(3-MeOsalen)]$_2$[Cr(CN)$_6$]·H$_2$O The phase transition occurs at $T_c = 11$ K.

Comparative Studies of Magnetic Properties

The magnetic properties of the series K[Mn(3-MeOsalen)]$_2$[M(CN)$_6$] (M = Co^{3+}, Fe^{3+}, Mn^{3+}, Cr^{3+}) are summarized in Table I. The Weiss constant θ reflects the nature and magnitude of the exchange (J) between the adjacent Mn^{3+} and M^{3+} ions and J is expressed by the sum of ferromagnetic and antiferromagnetic contributions, $J_{ij} = J_{ijF} + J_{ijAF}$.[4,5] The positive Weiss constants for [Mn$_2$Fe] and [Mn$_2$Mn] mean that, in that cases of Mn^{3+} ($e_g{}^1$, $t_{2g}{}^3$, S = 2) - Fe^{3+} ($t_{2g}{}^5$, S = 1/2) and Mn^{3+} ($e_g{}^1$, $t_{2g}{}^3$, S = 2) - Mn^{3+} ($t_{2g}{}^4$, S = 1) as the adjacent metal ion pairs, the exchange integrals (J_{MnFe} and J_{MnMn}) have a large ferromagnetic contribution arising from the interaction of the electron on an e_g orbital of Mn^{3+} and the electron(s) on a t_{2g} orbital of M^{3+} (M = Fe, Mn). The trend, $\theta_{\mathrm{Fe}} < \theta_{\mathrm{Mn}}$, is in accord with the increasing number of electrons in the t_{2g} orbitals of the M^{3+} ion. The [Mn$_2$Cr] has Mn^{3+} ($e_g{}^1$, $t_{2g}{}^3$, S = 2) - Cr^{3+} ($t_{2g}{}^3$, S = 3/2) as the adjacent metal ion pair and the Weiss constant indicates the magnetic exchange in the pair to be antiferromagnetic. Thus, the further increase in the number of unpaired electrons in the t_{2g} orbital of M^{3+} (t_{2g}^2 (Mn^{3+}) of [Mn_2Mn] ⇒ t_{2g}^3 (Cr^{3+}) of [Mn_2Cr]) does not lead to the enhancement of ferromagnetic contribution but gives rise to a dramatic change to a dominant antiferromagnetic contribution.

The interlayer magnetic behavior may depend upon the following three factors: (i) lattice fluctuations in the interlayer, (ii) the interlayer distance, (iii) the magnitude of ordered spin (dipole) in the layer (the theory of dipolar interaction). Factor (i) is most probable in two-dimensional layered compounds such as those described. Actually, a difference in interlayer magnetic interactions has been observed between crystal samples and powder samples of K[Mn(3-MeOsalen)]$_2$[Fe(CN)$_6$].[12] However, since the interlayer magnetic interaction is ferromagnetic in [Mn_2Cr] and that of [Mn_2Mn] is antiferromagnetic in spite of having similar interlayer environments with each other (see X-ray powder diffraction study), factor (iii) is expected, in particular, in such 2-D layered compounds having long range interlayer distances (the described compounds have the interlayer distances in the range of 12 - 14 Å).[6-9]

TABLE I The Magnetic Properties and Magnetism for K[Mn(3-MeOsalen)]$_2$[M(CN)$_6$] (M = Co^{3+}, Fe^{3+}, Mn^{3+}, Cr^{3+})

	Spin of M*1	θ (K)*2	Intralayer*3	Interlayer	Magnetism
Co^{3+}	0	-0.4	P	-	Paramagnet [10]
Fe^{3+}	1/2	+6.8	F	AF	Metamagnet [1,2]
Mn^{3+}	1	+16.2	F	AF	Metamagnet [3]
Cr^{3+}	3/2	-33.6	AF	F	Ferrimagnet

*1; $[M(CN)_6]^{3-}$. *2; from the plot of $1/\chi_M$ vs. *T*. *3; P = paramagnetic, F = ferromagnetic, AF = antiferromagnetic.

CONCLUSION

A series of bimetallic compounds of the general formula K[Mn(3-MeOsalen)]$_2$[M(CN)$_6$] (M = Co^{3+}, Fe^{3+}, Mn^{3+}, Cr^{3+}) has a similar 2-D network structure but their magnetic properties vary depending upon the nature of the metal ion of the $[M(CN)_6]^{3-}$ unit and the interlayer magnetic interaction. When M is Co^{3+} (S = 0), the observed magnetism is paramagnetic.[10] When M is Fe^{3+} (S = 1/2) or Mn^{3+} (S = 1), each assembly showed a metamagnetic nature owing to an intralayer ferromagnetic interaction and an interlayer antiferromagnetic interaction. The Weiss constant, reflecting the intralayer ferromagnetic interaction, is in the order, θ_{Fe} (+6.8 K) < θ_{Mn} (+16.2 K), in accord with the increase of unpaired electrons on the M^{3+}. When M is Cr^{3+} (S = 3/2), the observed bulk magnetism is ferrimagnet (T_c = 11 K) due to an intralayer antiferromagnetic interaction and an interlayer ferromagnetic interaction.

Acknowledgments

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