Anomalous Magnetic Properties of [K{Mn(3-MeO-salen)}$_2${Mn(CN)$_6$}]. A Metamagnet Exhibiting a Strong Negative Magnetization (3-MeOsalen = *N,N′*-Ethylenebis(3-methoxysalicylideneaminato)

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

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

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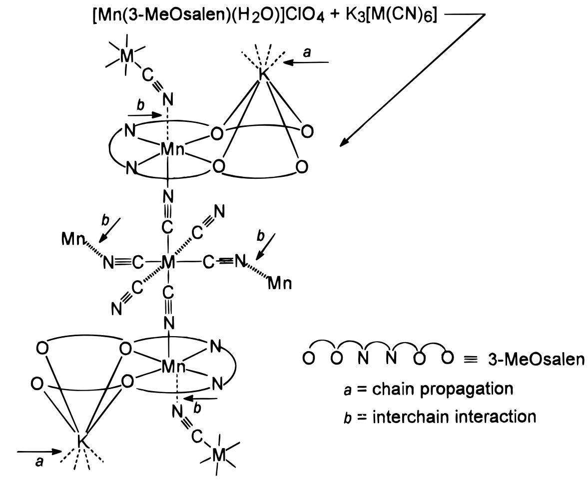
Many efforts have been directed in the last decade to the design of molecular-based magnetic materials exhibiting spontaneous magnetization.[1]

In this context, we have explored the assembling modes of [Mn^{III}(BS)]$^+$ [BS = tetradentate dianionic Schiff base] complexes and [Fe(CN)$_6$]$^{3-}$. Among the extended structures thus obtained, [K{Mn(3-MeOsalen)}$_2${Fe(CN)$_6$}]$_n$, **1**,[2] [salen = *N,N′*-ethylenebis(salicylideneaminato) dianion] has a two dimensional network derived from the cyclic octameric [Mn−NC−Fe−CN]$_4$ repeating unit (Scheme 1 and figure reported in the synopsis). This is a structure has a metamagnetic behavior derived from an intralayer ferromagnetic interaction and an interlayer weak antiferromagnetic interaction. The isostructural substitution of [Fe(CN)$_6$]$^{3-}$ by [Mn(CN)$_6$]$^{3-}$ in the same compound led to [K{Mn(3-MeOsalen)}$_2${Mn(CN)$_6$}]$_n$, **2**,[3,4] (Scheme 1 and figure reported in the synopsis) which has an analogous metamagnetic behavior with a Neel transition temperature T_N = 16 K. However, below 13.5 K, at low fields, **2** shows an anomalous negative magnetization. The corresponding diamagnetic susceptibility reaches very large values (higher than 10 cm^3 mol^{-1} at 10 Oe) which are several order of magnitude higher than the usual core diamagnetism, and this is an uncommon phenomenon.

Scheme 1



[K{Mn(3-MeOsalen)}$_2${M(CN)$_6$}]$_n$, M = Fe, **1**; M = Mn, **2**

The temperature dependencies of the effective magnetic moment μ_{eff} and the inverse of the magnetic susceptibility per Mn$_3$ measured under 800 Oe are shown in Figure 1. The μ_{eff} at room temperature, 7.80 μ_B, is slightly larger than the spin-only value of 7.48 μ_B for the magnetically dilute spin-system (S_{Mn} *hs*, S_{Mn} *ls*, S_{Mn} *hs*) = (2, 1, 2). This is probably due to an orbital contribution from the low-spin Mn(III) ion which has an orbitally degenerate $^3T_{1g}$ ground state for an ideal octahedral coordination. When the temperature is lowered, the magnetic moment increases gradually and then sharply below 20 K, finally decreasing below 16 K. The plot of $1/\chi_M$ *vs* T above 20 K obeys the Curie−Weiss law with $\theta = +16.2$ K. This positive value of the Weiss constant along with the absence of a minimum in the μ_{eff} *vs* T curve indicates a ferromagnetic interaction between high-spin Mn(III) and low-spin Mn(III) ions through a bridging CN group. The occurrence of a magnetic phase transition was studied by measuring the magnetization *vs* T at zero and very weak magnetic fields. The FCM (field cooled magnetization), RM (remnant magnetization) and ZFCM (zero-field cooled magnetization) curves *vs* T measured under a zero and a weak magnetic field of 10 Oe are given in Figure 2. When the temperature is lowered, the magnetization in the FCM curve shows a rapid increase below *ca.* 20 K, reaching a maximum (150 cm^3 mol^{-1} G) at 16 K. It then suddenly decreases, becomes strongly negative at ca. 13.5 K and finally reaches a saturation value of −120 cm^3 mol^{-1} G at 1.9 K. When the field was switched off at 1.9 K, the resulting RM curve shows a remnant magnetization (still equal to the saturation value of −120 cm^3 mol^{-1} G observed in the FCM curve) which, upon warming, becomes positive at 14 K, reaches a maximum of 45 cm^3 mol^{-1} G at 15 K, and then suddenly vanishes. The ZFCM curve was obtained by cooling the sample under zero field and warming it under 10 Oe. In the ZFCM curve, the magnetization value at 1.9 K is essentially zero and, upon warming, increases to become positive at 13 K, showing a peak

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[†] Università di Perugia.

[‡] University of Lausanne.

[§] Kyushu University.

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(3) Procedure for **2**: *Caution*! Perchlorate salts are potentially explosive and should only be handled in small quantities. To the ice-cooled solution of [Mn(3-MeOsalen)(H$_2$O)]ClO$_4$ (0.249 g, 0.5 mmol) in methanol (50 mL) was added a ice-cooled solution of K$_3$[Mn(CN)$_6$] (0.164 g, 0.5 mmol) in water (5 mL) in the ice-bath. The resulting solution was allowed to stand for 30 min in the ice-bath to give a reddish brown precipitate, which was collected by filtration, washed with 1:1 v/v methanol−water, and dried in vacuo. Anal. Calcd for **2**·H$_2$O, C$_{42}$H$_{38}$KMn$_3$N$_{10}$O$_9$: C, 48.94; H, 3.72; N, 13.59; Mn, 15.99. Found: C, 48.76; H, 3.66; N, 13.42; Mn, 16.22. IR (KBr): ν(C=N-(imine)), 1601, 1624 cm−1; ν(C−N(cyanide)), 2089, 2111 cm^{-1}. Mp: >300 °C. X-ray diffraction patterns of powdered samples were recorded on a Model RINT-2500 instrument from Rigaku Co. Ltd. with a graphite monochromator and Cu-Kα radiation (λ = 1.5418 Å) at 50 kV and 300 mA.

(4) The X-ray diffraction patterns of **1** and **2** were in general similar, indicating that these complexes have the same two-dimensional framework, although the interlayer spacing and the environment between two-dimensional sheets are different.

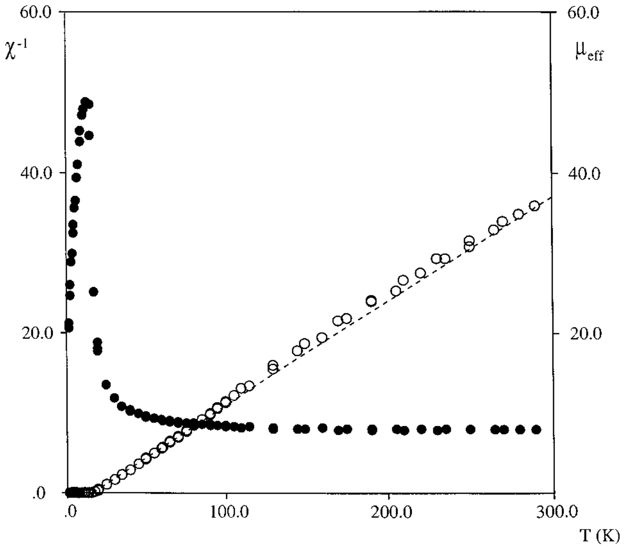

Figure 1. Plots of the effective magnetic moment (●) and the inverse of the magnetic susceptibility (○) for **2** per Mn_3 *vs* temperature.

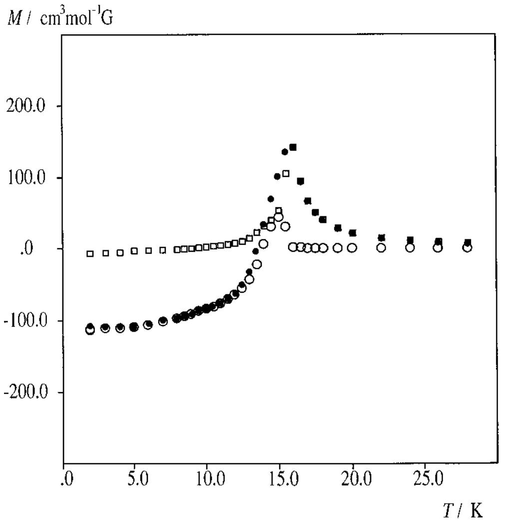

Figure 2. FCM (field-cooled magnetization) under 10 Oe, RM (remnant field) (○), and ZFCM (zero-field cooled magnetization) (■) under 10 Oe for **2**.

at ca. 16 K (150 cm^3 mol^{-1} G), and then slowly decreases following essentially the same behavior observed in the FCM curve.

The behavior above 13.5 K is analogous to that observed for compound **1** and typical of two dimensional metamagnetic systems.[2] The abrupt increase of the magnetization indicates the on-set of long range magnetic ordering due to the ferromagnetic coupling within each layer. The decrease below 16 K indicates the presence of interlayer antiferromagnetic interaction. More difficult to understand is the behavior below 13.5 K, where **2** exhibits an apparent diamagnetic moment.

To better characterize this anomalous diamagnetic behavior, FCM curves were also measured under 50, 75, 100, and 150 Oe (see Figure S1, Supporting Information). Only the M *vs* T curves taken under a field of 100 Oe or lower show a negative magnetization below ca. 13.5 K, while in the curve taken under a field of 150 Oe the magnetization remains always positive. Moreover, FCM curves taken at 300 and 800 Oe confirm the typical behavior of a metamagnetic system in the temperature range studied. Indeed, while the FCM curve taken under a field of 150 Oe goes suddenly to zero below the sharp peak around 16 K, the curve under 300 Oe has a peak at 16 K and then increases again, and the curve under 800 Oe saturates to 14000 cm^3 mol^{-1} G after the abrupt increase around 16 K. The field dependence of the magnetization up to 55 kOe was measured at 1.9, 6.0 and 12 K on a zero field cooled sample. On increasing the applied magnetic field at 1.9 K, the magnetization is close to zero below ca 500 Oe, increases rapidly to a plateau (about $M = 4\ N\mu_B$) around 3000 Oe and then increases gradually reaching a value of 8 $N\mu_B$ at the highest field measured (55 kOe). This value is lower than the magnetization saturation expected for this system (S_{Mn} *hs*, S_{Mn} *ls*, S_{Mn} *hs*) = (2, 1, 2), which is 10 $N\mu_B$ according to the equation $M_s = Ng\mu_B S$, and a field higher than 55 kOe is necessary for magnetic saturation. This behavior is typical of systems with a relevant anisotropy, like Mn(III) Schiff bases which are known to have a large zero-field splitting.[5] All these data confirm that at fields higher than 100 Oe compound **2** has essentially the same metamagnetic character of **1**, with a ferromagnetic intralayer interaction and an antiferromagnetic interlayer interaction. However, the magnetic behavior at very weak magnetic fields is completely different with **2** assuming negative values. Such an apparent diamagnetism is similar to that shown by some ferrimagnetic spinels, like Co_2VO_4[6] and Co_2TiO_4.[7] The magnetic behavior of these compounds is explained as due to the incomplete compensation of the magnetic moments of two antiferromagnetically aligned sublattices constituted by the same ions in crystallographically nonequivalent positions. The net magnetization is the sum of the magnetizations for the two sublattices, and a sign reversal can be observed because of different temperature dependencies of the individual sublattices magnetizations. An analogous behavior has been observed also for the cubic perovskite $LaVO_3$[8] and, more recently, for $NBu_4Fe^{II}Fe^{III}(C_2O_4)_3$,[9] which is the first example where such a phenomenon has been observed in a molecular-based magnet.

In spite of some similarities, the magnetic behavior of **2** is different from that seen in ferrimagnetic spinels, in $LaVO_3$ or in $NBu_4Fe^{II}Fe^{III}(C_2O_4)_3$ which all show ferrimagnetic interactions. Instead, compound **2** shows dominant ferromagnetic interactions above 16 K and is the first example in which such unusual negative magnetization is connected with metamagnetic behavior. Further studies are still in progress to clarify such an uncommon phenomenon.

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Supporting Information Available: FCM curves (Figure S1) and text giving comments on magnetic properties of complex **2** (2 pages). Ordering information is given on any current masthead page.

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