Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 05 Dec 2006.

To cite this article: Hisashi ōkawa , Naohide Matsumoto , Hiroko Tamaki & Masaakiohba (1993): Ferrimagnetic Mixed-Metal Assemblies $\{NBu_4[MFe(ox)_3]\}_x$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 233:1, 257-262

To link to this article: http://dx.doi.org/10.1080/10587259308054965

Mol. Cryst. Liq. Cryst. 1993, Vol. 233, pp. 257–262
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Printed in the United States of America

FERRIMAGNETIC MIXED-METAL ASSEMBLIES $\{NBu_4[MFe(ox)_3]\}_x$

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Abstract Hetero-metal assemblies, (NBu_4=tetra(n-butyl)ammonium ion; ox=oxalate ion; M(II)=Ni(**1**), Fe(**2**), Mn(**3**), Zn(**4**)) have been synthesized by the use of $[Fe(ox)_3]^{3-}$ as the building block. **1** and **2** are ferrimagnets of T_N=43 and 28 K, respectively. **3** is an antiferromagnet. **4** shows a paramagnetic behavior.

INTRODUCTION

The design of ferromagnetic materials based on metal complexes has been one of the most stimulating subjects in the past decade in inorganic chemistry field.[1-3] The generally adopted method is to prepare a ferromagnetic or ferrimagnetic chain and assemble the chain so as to achieve a three-dimensional ferromagnetic ordering. This method, however, suffers two serious problems: (1) the interchain magnetic interaction is often antiferromagnetic to afford three-dimensional antiferromagnetic ordering and (2) the ferromagnetic phase-transition temperature (T_C or T_N) remains low because of very weak interchain interaction even if ferromagnetic ordering is achieved over a lattice.

In order to avoid the problems in the method based on one-dimensional chains as the constituents, we have proposed a new synthetic strategy for complex-based ferromagnets.[4] Our method uses a D_3-symmetric η^3-complex as the building block with the hope to provide a three-dimensional network structure in one-pot reaction. In the previous study we adopted trisoxalatochromate(III) $[Cr(ox)_3]^{3-}$ as such a building block to obtain a series of ferromagnetic hetero-metal assemblies $\{NBu4[MCr(ox)3]\}_x$ which are presumed to have a network structure of alternatively arrayed Cr^{3+} and M^{2+} ions (Fig. 1, M'=Cr).[4] In this study we have prepared a series of mixed-metal assemblies $\{NBu_4[MFe(ox)_3]\}_x$ (M=Ni(**1**), Fe(**2**), Mn(**3**), Zn(**4**)) by the use of trisoxalatoferrate(III) $[Fe(ox)_3]^{3-}$ as the building block. Their magnetic properties are described.

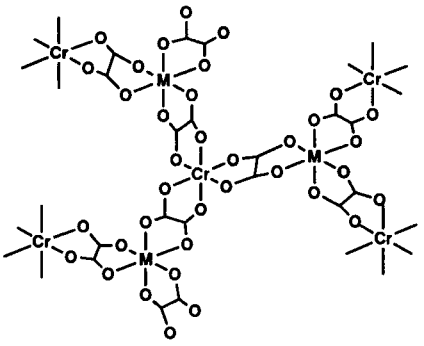

FIGURE 1 Proposed structure of $\{NBu_4[MCr(ox)_3]\}_x$.

PREPARATION OF $\{NBu_4[MFe(ox)_3]\}_x$

An aqueous solution (40 cm^3) of $K_3[Fe(ox)_3]\cdot 3H_2O$ (3 mmol) and an aqueous solution (15 cm^3) of tetra(n-butyl)ammonium bromide (4.5 mmol) were mixed at 0 °C. To the resulting solution was added an aqueous solution (ca. 10 cm^3) of a metal(II) chloride (2 mmol) to cause immediate precipitation of microcrystals. They were collected by filtration, washed with water, and dried in vacuo.

TABLE I Color and analytical data of $\{NBu_4[MFe(ox)_3]\}_x$.

M(II)		color	Found % (Calcd %) C	H	N	Fe	M
Ni	(1)	green	42.35 (42.55)	6.02 (5.84)	2.28 (2.26)	9.9 (9.0)	9.9 (9.5)
Fe	(2)	deep green	42.96 (42.74)	5.99 (5.87)	2.24 (2.27)	17.6 (18.1)	
Mn	(3)	pale yellow	42.74 (42.81)	5.86 (5.88)	2.24 (2.27)	8.4 (9.1)	9.2 (8.9)
Zn	(4)	yellow green	41.16 (42.09)	5.78 (5.78)	2.28 (2.23)	9.7 (8.9)	10.5 (10.4)

The mixed-metal assemblies are sensitive to light. The parent complex $K_3[Fe(ox)_3]\cdot 3H_2O$ shows ν(C=O) bands of simply chelated ox group at 1720 and 1685 cm^{-1} whereas **1-4** each shows one ν(C=O) band of bridging ox group at 1630 cm^{-1}.

MAGNETISM

Cryomagnetic properties of **1-4** were studied in the temperature range of 4.2-100 K by the use of a HOXAN HSD-2000 SQUID susceptometer (applied field 1×10^{-2} T) and in the range of 80-290 K by the use of a Faraday balance (applied field 5×10^{-1} T).

$\{NBu_4[NiFe(ox)_3]\}_X$ (**1**). The magnetic behavior of **1** is shown in Fig. 2 in the forms of χ_M vs. T, χ_M^{-1} vs. T, and μ_{eff} vs. T plots per NiFe unit. The magnetism obeys the Curie-Weiss law ($\chi_M^{-1}=(T-\theta)/C$) with θ =-80 K in the range 130-290 K but deviates from the law below 130 K. The effective magnetic moment per NiFe is 6.18 μ_B at room temperature that is slightly smaller than the spin-only value for Ni(II) (S=1)-Fe(III) (S=5/2). The moment decreases with lowering of temperature down to the minimum 5.01 μ_B at 74 K, increases sharply upto the maximum 10.3 μ_B at 27 K, and decreases again. The round minimum in the μ_{eff} vs. T curve is characteristic of ferrimagnets.[5] To confirm the magnetic phase-transition the temperature-dependences of magnetization of **1** were measured under weak magnetic field (3G) (see Fig. 3). The field cooled magnetization (FCM) obtained by cooling the sample under 3 G showed a rapid increase in magnetization below 32 K. When the field was switched off, a remnant magnetization was observed which vanished at 28 K upon warming. The zero-field cooled magnetization (ZFCM : cooling in zero field and warming under 3 G) showed a maximum at T_N=28 K. This complex shows a "spin-glass" like phenomenon below 26 K.

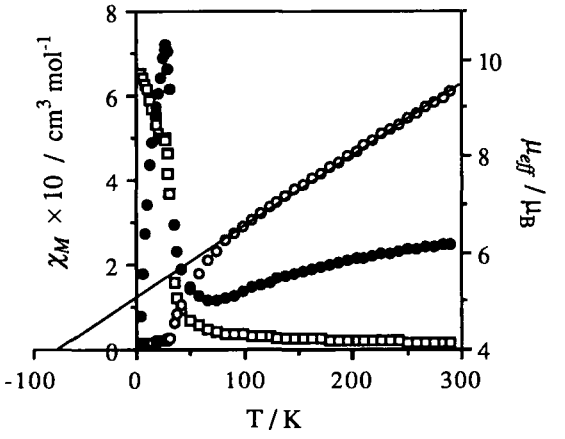

FIGURE 2 Temperature-dependences of χ_M(□), χ_M^{-1} (○), and μ_{eff} (●) per NiFe unit of $\{NBu_4[NiFe(ox)_3]\}_X$.

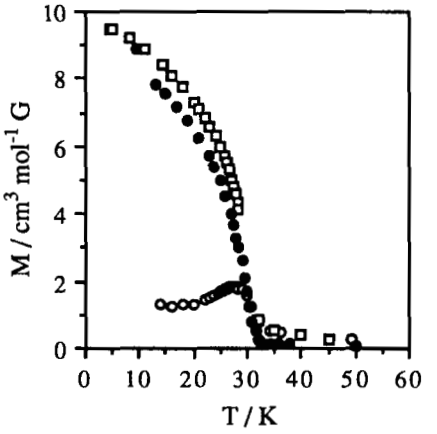

FIGURE 3 Temperature-dependences of the molar magnetization for $\{NBu_4[NiFe(ox)_3]\}_x$: field cooled magnetization (○), zero-field cooled magnetization (□), and remnant magnetization(●).

$\{NBu_4[FeFe(ox)_3]\}_x$ (**2**). The magnetic behavior of **2** resembles that of **1**. The effective magnetic moment per FeFe is 7.24 μ_B at room temperature that is smaller than the spin-only value 7.68 μ_B for Fe(II) (S=2)-Fe(III) (S=5/2). The moment decreases with lowering of temperature down to the minimum 4.50 μ_B at 48 K, increases sharply up to the maximum 18.1 μ_B, and decreases again below this temperature (see Fig. 4).

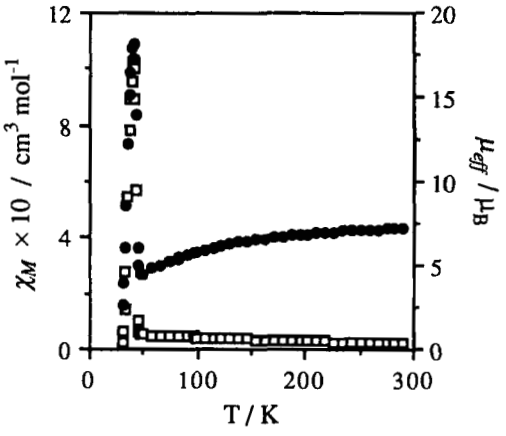

FIGURE 4 Temperature-dependences of χ_M(□) and μ_{eff} (●) per $Fe^{II}Fe^{III}$ unit of $\{NBu_4[FeFe(ox)_3]\}_x$.

Magnetization measurements have revealed a magnetic phase-transition at T_N=43 K for this complex (Fig. 5). This complex also shows a "spin-glass" like phenomenon below 40 K. The origin for the very unique spin-glass like phenomenon of **1** and **2** remain to be studied in future.

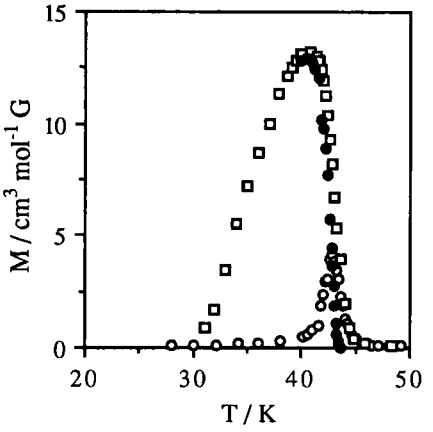

FIGURE 5 Temperature-dependences of the molar magnetization for $\{NBu_4[FeFe(ox)_3]\}_x$: field cooled magnetization (○), zero-field cooled magnetization (□), and remnant magnetization(●).

$\{NBu_4[MnFe(ox)_3]\}_x$ (**3**). The μ_{eff} of **3** is 7.47 μ_B at 290 K, that is considerably lower than the spin-only value 8.37 μ_B for Mn(II)(S=5/2)-Fe(III)(S=5/2), and decreases monotonously down to 1.32 μ_B at 4.2 K (Fig. 6). This fact clearly indicates that the spins of the neighboring Mn(II) and Fe(III) ions are antiferromagnetically coupled to afford a three-dimensional antiferromagnet. This adds a support to that the magnetic interaction between the nearest neighbors of **1** and **2** is antiferromagnetic.

$\{NBu_4[ZnFe(ox)_3]\}_x$ (**4**). The magnetic moment of **4** at room temperature is 5.7 μ_B. Further, it is found that the moment is essentially constant in the temperature range 4.2-300 K (Fig. 6). This fact clearly demonstrates that the alternative array of Fe(III) and M(II) ions is exactly achieved over the three-dimensional lattice.

It is to be noticed that the magnetic phase-transition temperatures T_N of the ferrimagnets **1** and **2** are significantly high compared with the corresponding ferromagnets $\{NBu_4[NiCr(ox)_3]\}_x$ (T_C=14 K) and $\{NBu_4[FeCr(ox)_3]\}_x$ (12 K), respectively.

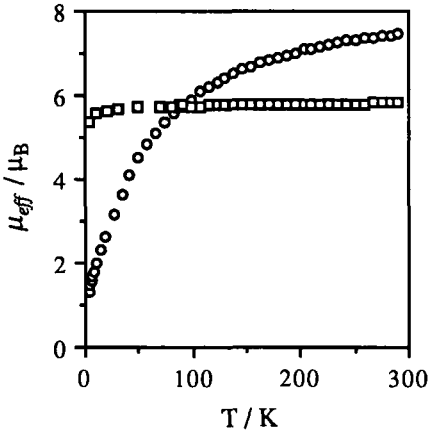

FIGURE 6 Temperature-dependences of μ_{eff} per $M^{II}Fe$ unit of $\{NBu_4[MnFe(ox)_3]\}_x$ (○) and $\{NBu_4[ZnFe(ox)_3]\}_x$ (□).

Recently we have shown that the T_C of $\{NBu_4[MCr(ox)_3]\}_x$ is governed by the spin-exchange integral J between the nearest neighbors, M(II) and Cr(III), and the spins of the metals, S_M and S_{Cr}.[6] All these findings strongly suggest that the magnetic phase-transition temperature (T_C or T_N) of the hetero-metal assemblies $\{NBu_4[M(II)M'(III)(ox)_3]\}_x$ can be improved when the combination of metal ion pair, M(II) and M'(III), are properly chosen.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Area "Molecular Magnetism" (Area No.228 / 04242104) from the Ministry of Education, Science and Culture, Japan.

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