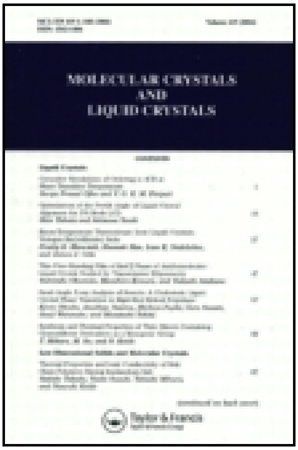

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Zhongze Gu [a], O. Sato [b], T. Iyoda [b], K. Hashimoto [a] [b] & A. Fujishima [a]

[a] Department of Applied Chemistry, The University of Tokyo, 7-3-1 Kongo Bunkyo-Ku, Tokyo, 113, Japan

[b] Kanagawa Academy of Science and Technology, in Tokyo Institute of Polytechnics, 1583 Iiyama, Atsugi, Kanagawa, 243-02, Japan

Version of record first published: 04 Oct 2006.

To cite this article: Zhongze Gu , O. Sato , T. Iyoda , K. Hashimoto & A. Fujishima (1996): Syntheses and Magnetic Properties of Dye Included Organometallic Magnets: DAMS[MCr(ox)$_3$], Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 286:1, 147-152

To link to this article: http://dx.doi.org/10.1080/10587259608042279

Mol. Cryst. Liq. Cryst., 1996, Vol. 286, pp. 147–152
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SYNTHESES AND MAGNETIC PROPERTIES OF DYE INCLUDED ORGANOMETALLIC MAGNETS: DAMS[MCr(ox)3]

ZHONGZE GU*, O.SATO†, T.IYODA†, K.HASHIMOTO*†, and
A.FUJISHIMA*
*Department of Applied Chemistry, The University of Tokyo, 7-3-1 Hongo
Bunkyo-Ku, Tokyo 113, Japan
†Kanagawa Academy of Science and Technology, in Tokyo Institute of
Polytechnics, 1583 Iiyama, Atsugi, Kanagawa 243-02, Japan

Abstract A series of dye-included metal complex-based magnets, DAMS[MCr(ox)3] ($DAMS^+$ = 4-[2-(4-dimethylaminophenyl)ethenyl]-1-methylpyridinium cation; M^{2+}=Mn^{2+}, Fe^{2+}, Ni^{2+}; ox^{2-}=Oxalate Ion), were synthesized. In these compounds different kinds of metal cations are bridged to each other by ox^{2-} ions. The compounds have a layered-structure and molecules of $DAMS^+$ are enclathrated between the layers. Field-cooled magnetization (FCM) measurement showed that these compounds exhibit magnetic phase transition at 10K, 14K, and 18K respectively.

INTRODUCTION

The design of molecular-based magnets is attracting considerable interest recently. Current research in this field aims not only to improve magnetic properties, but also to achieve novel effects. We have reported several types of such magnets based on Prussian Blue analog.[1-3] In these magnets, magnetic properties can be controlled by optical or electrochemical stimuli. By taking advantage of an inclusion compound, we set out to prepare a new kind of magnets with optical properties.

Inclusion compound is composed of host and guest molecules. The guest molecules are enclathrated into the voids or tunnels of the host lattice. The host material we selected is a metal oxalate. Oxalate ion (ox^{2-}) is a well-known mediator for both antiferromagnetic and ferromagnetic interaction between identical or different metal cations and has been extensively used as a bridge for spin interaction to construct molecular-based magnets.[4] Since a compound, $A^{I}[M_1^{II}M_2^{III}(ox)_3]$, in which M_1^{II} and M_2^{III} are bridged by ox^{2-}, has a layered-structure (Figure 1), it can be utilized as a host compound. Thus, it is possible to include functional molecules into the magnetic host material formed by metal oxalate and to give an additional properties for this compound. Here, we report syntheses and magnetic properties of a series of dye inclusion metal oxalate: $DAMS[MCr(ox)_3]$ ($DAMS^+$ = 4-[2-(4-dimethylaminophenyl) ethenyl]-1-methylpyridinium cation; M^{2+}= Mn^{2+}, Fe^{2+}, Ni^{2+}; ox^{2-}=Oxalate Ion).

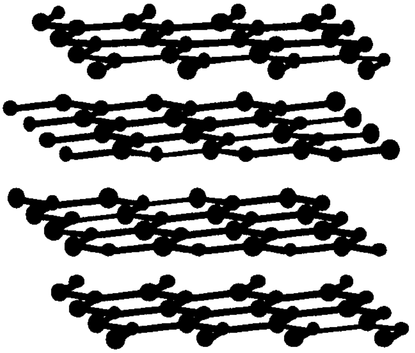

FIGURE 1 Layered structure[5] of $NBu_4[MnCr(ox)_3]$ in which large spheres are Mn^{2+} and small spheres are Cr^{3+}. For clarity, ox^{2-} is represented by a line between Mn^{2+} and Cr^{3+}, and the molecules of NBu_4 between the layers are omitted.

EXPERIMENT

Physical Measurement

IR spectra were measured with an FTS-40A spectrophotometer (Bio-RAD). UV-visible spectra were recorded by the diffuse-reflectance technique with a UV-3100PC spectrophotometer (SHIMADZU). Magnetic susceptibilities were measured with a super-conducting quantum interference device (SQUID) magnetometer (QUANTUM DESIGN MPMS-5S).

Syntheses

Compounds of $DAMS[MCr(ox)_3]$ (M^{2+}=Mn^{2+}(1), Fe^{2+}(2), Ni^{2+}(3)) were prepared by mixing a methanol solution of $DAMS^+$ with an aqueous solution of $K_3[Cr(C_2O_4)_3]•3H_2O$ and metal(II) chloride (molar ration=1:1:1.5). All of the compounds are obtained as fine powders. [Calculated composition for compound (1) C: 43.30 N: 4.59 H: 3.11, Found: C: 44.86 N: 4.89 H: 2.11; Calculated composition for compound (2) C: 43.23 N: 4.58 H: 3.11, Found: C: 45.90 N: 5.01 H: 2.68, Calculated composition for compound (3) C: 43.03 N: 4.56 H: 3.10 Found: C: 45.72 N: 5.06 H: 2.05.]

RESULTS AND DISCUSSION

IR spectra of these compounds show υ(CO) and δ(CO) at 1645cm^{-1} and 806cm^{-1} while υ(CO) and δ(CO) for oxalate group in $K_3[Cr(ox)_3]{\bullet}3H_2O$ appear at 1713cm^{-1} and 802cm^{-1}. Such shifts indicate all of the oxalate ions are bridged to metal cations.[6] No apparent shift for DAMS$^+$ was observed.

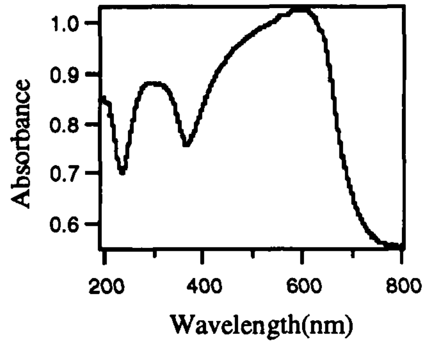

FIGURE 2 UV-visible absorbance spectrum of DAMS[MnCr(ox)3

In UV-visible spectra (Figure 2) a broad absorption band in the region of 364nm–800nm with a maximum at ca. 580nm was observed. This absorbance is composed of characteristic d–d transitions at 420nm, 580nm, and 698nm for six-coordinated Cr^{III}, and π–π* transition at ca.490nm for DAMS$^+$. Another absorption band with a maximum at ca. 280nm is ascribed to the higher transition localized in pyridinium and benzene moieties of DAMS$^+$.[7] From these results it is reasonable to conclude that $DAMS[MCr(ox)_3]$ has a equivalent structure with $NBr_4[MnCr(ox)_3]$ (NBu_4^+ = Tetra(n-butyl)ammonium cation) reported previously.[5] That is to say, $[MCr(ox)_3{}^{2-}]_x$ forms a layered network structure as shown in Figure 1 and the DAMS$^+$ molecules are enclathrated between the layers.

TABLE 1: Magnetic properties of $DAMS[MCr(ox)_3]$ (M^{2+}=Mn^{2+}, Fe^{2+}, Ni^{2+})

	μ_{eff}/μ_B[a]	$\mu_{eff}(300K)/\mu_B$[b]	$M_S(F)/N\mu_B$[c]	$M_S(AF)/N\mu_B$[c]	$M(50kG)/N\mu_B$[d]	T_C/K	θ/K
MnCr	7.07	6.33	8	2	3.17	10	-1.6
FeCr	6.24	6.15	7	1	3.71	14	14.6
NiCr	4.58	4.9	5	1	1.67	18	10.1

a) spin only value of effective magnetic moment, b) experiment value calculated by $\mu_{eff} = 2.828(\chi T)^{1/2}$ at 300K c) saturation magnetization expected with ferro- (F) and antiferro- (AF) exchange interaction between metals cations bridged by ox^{2-} (N: Avogadro's number), d) magnetization in 50kG at 5K.

Magnetic properties of these compounds were measured in 2K–300K (Table 1). Effective magnetic moments (μ_{eff}) per molecular unit of $DAMS[MCr(ox)_3]$ at 300K calculated by the equation $\mu_{eff} = 2.828(\chi T)^{1/2}$ are (1) 6.33μ_B (μ_B: Bohr magneton), (2) 6.15μ_B, and (3) 4.9μ_B. Assuming that all the metal cations take high-spin states (S_{Cr}=3/2, S_{Mn} = 5/2, S_{Fe} = 4/2, S_{Ni} = 2/2), the μ_{eff} expected for (1), (2) and (3) are 7.07μ_B, 6.24 μ_B, and 4.58 μ_B, respectively. They are almost consistent with the experimental values. Plots of field-cooled magnetization (FCM) versus temperature at

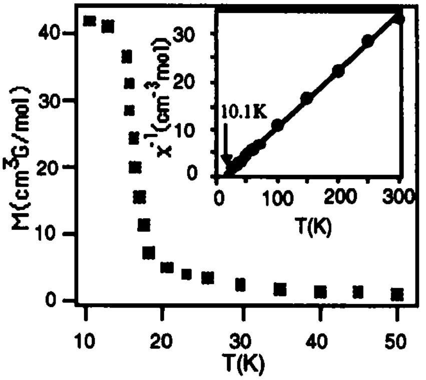

FIGURE 3 FCM for DAMS[NiCr $(ox)_3$]. Insert shows the temperature dependence of inverse susceptibility $1/\chi$.

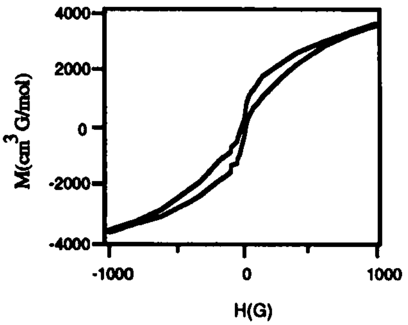

FIGURE 4 Plot of Hystersis for DAMS[NiCr$(ox)_3$] at 5K.

magnetic field H=5G displayed abrupt breaks at T_C (magnetic phase transition temperature)= 10K, 14K, and 18K for (1) , (2), and (3) respectively (Figure 3). Magnetic hystersises appear below T_C. As an example, the hystersis of DAMS[NiCr$(ox)_3$] at 5K is shown in Figure 4. The remnant magnetization of this compound is 268.47 cm^3 G/mol which is about 3% of the saturation magnetization. Coercive field of the compound is 13.4 G. Weiss temperatures (θ) for (1), (2), and (3) calculated from Curie-Weiss formula, $1/\chi=C/(T-\theta)$, are -1.6K, 14.6K, and 10.1K, respectively.

In order to analyze the magnetic properties in detail, field dependence of magnetizations were also measured. As shown in Figure 5, the magnetizations of (1) and (3) almost saturate at 50kG, but no saturation for (2) can be observed at 50kG. Magnetizations for (1) and (3) at 50kG are 3.17Nμ_B (N: Avogadro's number) and 1.67Nμ_B. The magnetizations at 50kG are larger than those expected from antiferromagnetic alignment of the spins in metal cations, but smaller than those expected from ferromagnetic interaction.

In order to elucidate the magnetic interaction in these compounds, it is worth to compare the magnetic properties of DAMS[MCr$(ox)_3$] with those of NBu_4[MCr$(ox)_3$] reported by Tamaki et al.[5] (Table 2). Weiss temperatures, θ, of DAMS[MCr$(ox)_3$] are smaller than those of NBu_4[MCr$(ox)_3$]. In other words, the exchange interactions, J, in (1), (2), and (3) are smaller compared with the corresponding NBu_4[MCr$(ox)_3$]. Furthermore, the θ of compound (1) is negative, in contrast to positive value for NBu_4[MnCr$(ox)_3$]. The relatively small values of J for DAMS[MCr$(ox)_3$] can not be simply attributed to the decrease of the magnetic interaction between metal ions bridged by ox^{2-}. Because the Tc values of DAMS[$MCr(ox)_3$] are increased. In addition, the dominance of antiferromagnetic interaction over ferromagnetic one in compound (1) can not be explained only by the intra-layer magnetic interaction in Mn^{II}-ox-Cr^{III}, since the d_{xy}-d_{xy} exchange interaction between Mn^{II} and Cr^{III} is absent for Mn^{II}-ox-Cr^{III}.[8]

TABLE 2: Magnetic properties[4] of $NBu_4[MCr(ox)_3]$ (M^{2+}=Mn^{2+}, Fe^{2+}, Ni^{2+})

	S_M[a]	S_T[b]	$M_S/N\mu_B$[c]	T_C/K	θ/K
MnCr	5/2	8/2	7.74	6	7.2
FeCr	2	7/2	6.71	12	18.2
NiCr	1	5/2	4.94	14	19.0

a) spin quantum number of M. b) spin quantum number for a unit formula of $NBu_4[MCr(ox)_3]$. c) saturation magnetization.

Such included cation dependence of the magnetic properties has also been reported in $(XBu_4)FeFe(ox)_3$ (X=N, P).[9] Powder X-ray diffraction patterns show that the distances between $\{[MCr(ox)_3]^{2-}\}_x$ layers are expanded, although the crystal structures are identical with those of $NBu_4[MCr(ox)_3]$. Thus, it can be concluded that the interlayer interaction play an important role in the change of the magnetic properties of these compounds. As to the compounds of DAMS[$MCr(ox)_3$], the exchange interaction can be expressed as:

$$J \propto \sum J(\text{Intra}) + \sum J(\text{Inter})$$

where J(Intra) is the intralayer ferromagnetic exchange interaction between the metal ions linked by ox^{2-} and the J(Inter) is the interlayer interaction which is antiferromagnetic for compounds (1), (2) and (3). It is apparent that the enhancement of the interlayer antiferromagnetic interaction makes the values of J and θ decrease. Furthermore, the enhancement of interlayer interaction causes a three-dimensional magnetic interaction, so that the magnetic phase transition temperatures, T_C, of DAMS[$MCr(ox)_3$] are increased.[10]

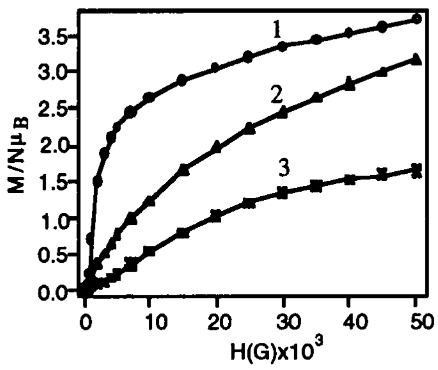

FIGURE 5 Field dependence of magnetizations for DAMS[$MCr(ox)_3$] (M = (1) Mn, (2) Fe, (3) Ni).

Such explanation for the magnetic properties of DAMS[$MCr(ox)_3$] is supported by the saturation magnetization. As is shown above, the saturation magnetizations of (1), (2) and (3) are intermediate between values calculated for ferro- and ferri-magnetism. Such phenomenon is always the case in layered-compound with antiferromagnetic interlayer interaction.[10, 11]

CONCLUSION

A series of dye-enclathrated magnets, DAMS[MCr(ox)3], are synthesized. Magnetic interaction in $\{[MCr(ox)_3]^{2-}\}_x$ can be described by intra- and inter-layer interaction. The interlayer interaction is significantly changed by the inclusion of DAMS. Since DAMS has a large second and third order nonlinear susceptibility, high non-linear optical response can be anticipated.

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