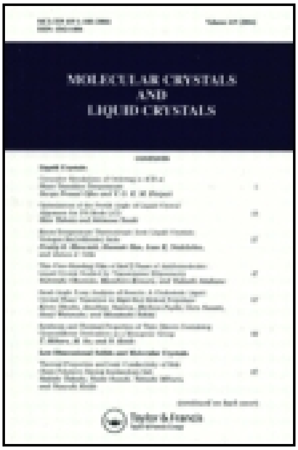

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Magnetism of a New oxalate-BRIDGED Metal Complex $\{NPr_4[MnCr(ox)_3]\}_x$

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MAGNETISM OF A NEW OXALATE-BRIDGED METAL COMPLEX $\{NPr_4[MnCr(ox)_3]\}_x$

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Abstract The oxalate-bridged complex $\{NPr_4[MnCr(ox)_3]\}_x$ (**1**) was prepared and its magnetic properties were studied, where NPr_4^+ = tetra(*n*-propyl)ammonium ion, ox^{2-} = oxalate ion. X-ray powder pattern measurements suggested that the distance between the layers consisting of alternate array of Mn^{2+} and Cr^{3+} through ox^{2-} ligands is shorter in **1** than $\{NBu_4[MnCr(ox)_3]\}_x$ (**2**) (NBu_4^+ = tetra(*n*-butyl)ammonium ion). The magnetic transition temperature of **1** ($T_c = 6.3 \pm 0.2$ K) determined from ac magnetic measurements was, however, almost the same as the T_c reported for **2**. In contrast with the case of **2**, compound **1** showed a normal magnetization curve which saturates rapidly with the increase of magnetic field (below 10 kG).

INTRODUCTION

A series of mixed-metal assemblies $\{NBu_4[M(II)M'(III)(ox)_3]\}_x$ were reported by Ōkawa et al. to exhibit bulk magnetism, where NBu_4^+ = tetra(*n*-butyl)ammonium ion, ox^{2-} = oxalate ion.[1-4] Ferromagnets,[1,2] ferrimagnets,[3,4] an antiferromagnet[3,4] and

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paramagnets[2-4] can be prepared according to the combinations of M(II) and M'(III). It seems also important to elucidate the role of the quarternary cation in order to modify the magnetic structure of this molecular-based system.[5-7] We have prepared a complex containing tetra(*n*-propyl)ammonium ion (NPr_4^+) in place of NBu_4^+, $\{NPr_4[MnCr(ox)_3]\}_x$ (**1**), and compared its magnetic properties with those of the ferromagnet $\{NBu_4[MnCr(ox)_3]\}_x$ (**2**).

EXPERIMENTAL

Compound **1** was obtained as green microcrystals by the reaction of $K_3[Cr(ox)_3]\cdot3H_2O$ with $MnCl_2\cdot4H_2O$ in the presence of NPr_4Br. Anal. Calcd for $C_{18}H_{28}NO_{12}CrMn$: C, 38.79; H, 5.06; N, 2.51; Cr, 9.33; Mn, 9.86. Found: C, 38.79; H, 5.18; N, 2.57; Cr, 9.20; Mn, 9.73. The X-ray powder diffraction patterns were recorded on a RAX01 diffractometer (Rigaku) using the CuKα radiation with a graphite monochrometer. The lattice parameters were obtained from refinement of 19 major reflections by employing the TREOR 84 analysis program. The temperature dependence of magnetic susceptibility under 4.65 kG was measured by a Faraday balance consisting of a Cahn 2000 microbalance in the range of 4.2-290 K.[8] A Quantum Design's MPMS2 SQUID magnetometer was used for the measurements of the field cooled magnetization (10 G), zero-field cooled magnetization, magnetization curve between ±10 kG, and ac magnetic susceptibility.

RESULTS AND DISCUSSION

A two-dimensional network structure was reported for **2** from a single crystal X-ray study.[9] Honeycomb-like layers are formed by the alternate array of Mn^{2+} and Cr^{3+} ions through ox^{2-} ligands in the lattice, and the hexagonal lattice parameters of **2** were obtained as $a = 9.414(5)$ Å and $c = 53.662(6)$.[9] The X-ray powder diffraction profile of **1** was indexed also on a hexagonal cell with the parameters of $a = 9.40$ Å and $c = 49.23$ Å. The observed density of **1** (1.49 g/cm^3) was in good agreement with the calculated density (1.474 g/cm^3, $Z = 6$). The shorter c value of **1** compared with that of **2** suggests a shortening of the distance between the basic layers as a result of the

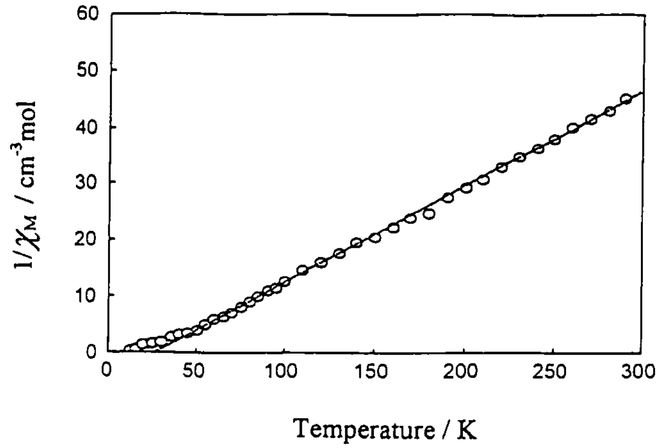

FIGURE 1 Plot of the temperature dependence of the reciprocal magnetic susceptibility ($1/\chi_M$) per MnCr unit for **1**.

substitution of NBu_4^+ in **2** with the smaller NPr_4^+.[9]

The plot of $1/\chi_M$ vs. T for **1** under 4.65 kG are shown in Figure 1, where χ_M is the dc magnetic susceptibility per MnCr unit. Above *ca.* 50 K, the plot was nearly linear and obeyed the Curie-Weiss law with a positive Weiss constant θ = 27.0 K, which indicates a ferromagnetic interaction and is somewhat larger than the θ reported for **2** (7.2 K).[2] A deviation of the plot from a straight line was observed below *ca.* 50 K.

The field-cooled magnetization (FCM) and zero-field cooled magnetization (ZFCM) of **1** were measured under a weak dc magnetic field (10 G). As shown in Figure 2, both of the FCM and ZFCM increased rapidly below *ca.* 10 K and the ZFCM showed a maximum around 6 K; this indicates the magnetic phase transition of **1** from a paramagnet to ferromagnet by lowering the temperature.

In order to determine precisely the Curie point (T_c) of **1**, the real (χ_M') and imaginary (χ_M'') parts of ac susceptibility (Hac = 1 G, frequency 210 Hz) under zero dc field were measured as shown in Figure 3. From the peak position of the derivative curve of χ_M' with respect to temperature, the T_c of **1** was obtained to be 6.3±0.2 K, where χ_M'' shows also an anomaly. This value of T_c is almost the same as that (6 K) estimated for **2** from the temperature dependence of dc magnetization,[2] while some extent of difference in θ was observed between **1** and **2** as mentioned above. This result would mean that the shortening of the interlayer distance caused by the substitution of NBu_4^+ with NPr_4^+ is not effective to vary the T_c appreciably. A similar T_c (5.9 K) was also reported for $\{P(Ph)_4[MnCr(ox)_3]\}_x$, where $P(Ph)_4^+$ = tetraphenylphosphonium ion.[6]

The magnetization curve of **1** was measured at 1.8 K in the magnetic field range of ±10 kG. In the case of **2**, it was reported that the magnetic field necessary to reach the saturation is fairly large (> 40 kG), and a spin canting mechanism due to the long-range structural disorder was proposed.[2] However, the magnetization of **1** was observed to saturate rapidly with the increase of magnetic field (below 10 kG), as

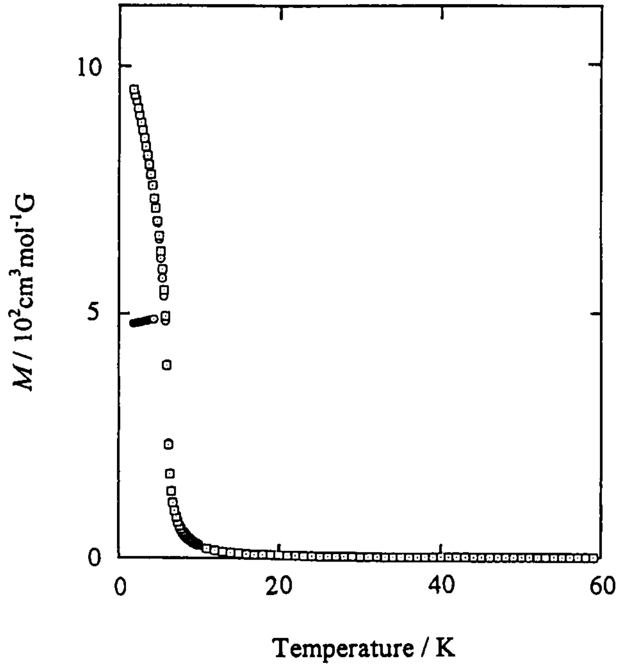

FIGURE 2 Plot of the temperature dependence of the magnetization M for **1**: (□) field cooled magnetization (FCM) (10 G), (○) zero-field cooled magnetization (ZFCM).

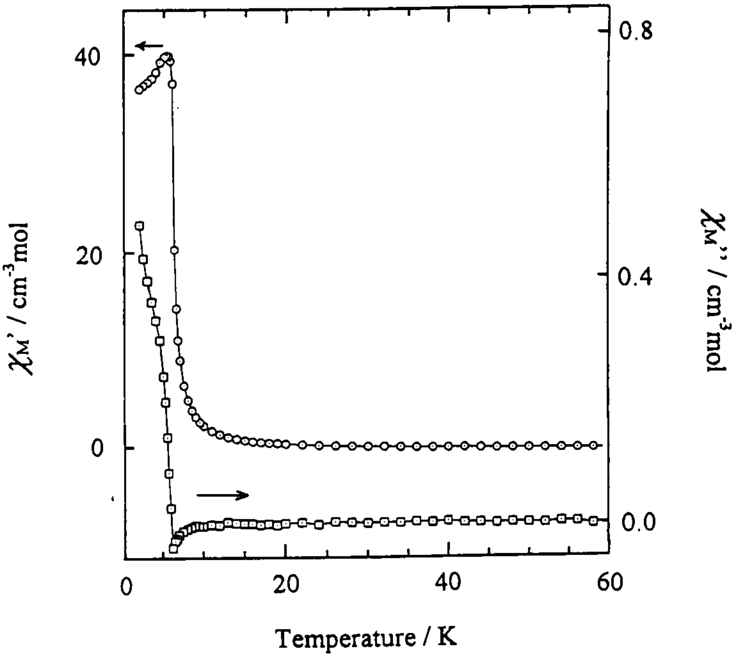

FIGURE 3 Plots of the temperature dependences of the real (χ_M') and imaginary (χ_M'') components of the ac susceptibility for **1** (1 G, 210 Hz).

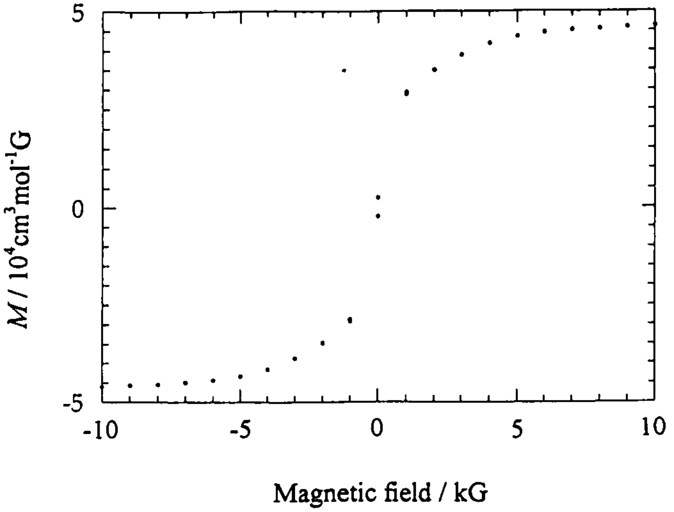

FIGURE 4 Magnetization curve of **1** at 1.8 K.

shown in Figure 4. The magnetization under 10 kG was determined to be 4.6×10^4 $cm^3mol^{-1}G$, which is compatible with the expected value (4.5×10^4 $cm^3mol^{-1}G$) for a ferromagnetic alignment of high-spin Mn^{2+} and Cr^{3+} ions. The above results suggest that the extent of the lattice disorder is affected by the kinds of the quarternary cation and the disorder in **1** is not apparent compared with the case of **2**. Compound **1** showed a small coercive force (100 G) which is somewhat larger than that of **2** (20 G).[2] The effects of other quartenary cations having different alkyl chain lengths on the behavior of this magnetic system are currently being investigated.

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