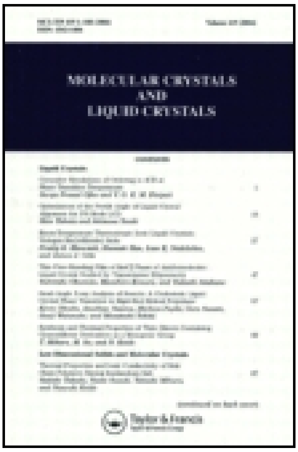

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Mössbauer Study of the Spin Direction in Oxalate-Bridged Mn(II)-Fe(III) Complexes

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Oxalate-bridged mixed metal assemblies A[Mn(II)Fe(III)(ox)$_3$] with large templating cations, $A^+ = P(C_6H_5)_4{}^+$ and $As(C_6H_5)_4{}^+$, exhibited a spin direction almost perpendicular to the honeycomb layers consisting of the alternate array of Mn(II) and Fe(III) ions through oxalate ligands. On the other hand, the spins were aligned parallel to the basal layers in the compound with the small cation, $NPr_4{}^+$. A variation of ca. 70° in spin direction was observed for mixed crystals NPr$_4$[Mn(II)Fe(III)$_x$Cr(III)$_{1-x}$(ox)$_3$].

Keywords: Mössbauer spectroscopy; oxalates; spin direction

INTRODUCTION

^{57}Fe Mössbauer spectroscopy has provided significant information regarding the electronic and magnetic structures of the iron-containing members of the molecule-based magnets A[M(II)M'(III)(ox)$_3$], where A^+ = organic cations such as quarternary ammonium and ox^{2-} = oxalate ion[1-8]. The A[M(II)M'(III)(ox)$_3$] compounds have the same basic structure that is constructed by the honeycomb layers consisting of the alternate array of M(II) and M(III)' ions through ox^{2-} ligands, being separated by the templating counter ions A^+ [9]. The ^{57}Fe Mössbauer investigations of NBu$_4$[M(II)M'(III)(ox)$_3$] ($NBu_4{}^+$ = tetra(*n*-butyl) ammonium ion)[1-8] revealed that the compounds containing a metal ion with single ion anisotropy, such as $NBu_4[Fe(II)Cr(III)(ox)_3]$[1,2], $NBu_4[Fe(II)Fe(III)(ox)_3]$[1] and $NBu_4[Co(II)Fe(III)(ox)_3]$[8], exhibit a spin direction parallel to the basal honeycomb layers. On the other hand, the directions in the compounds consisting of only magnetically-isotropic metal ions, such as $NBu_4[Ni(II)Fe(III)(ox)_3]$[4] and ^{57}Fe(III)-doped $NBu_4[Mn(II)Cr(III)(ox)_3]$[6], are nearly perpendicular to the basal layers. $NBu_4[Mn(II)Fe(III)(ox)_3]$ (**1**) was found to be an exception, which gives an intermediate direction of spin alignment[4]. In the present work, we have measured ^{57}Fe Mössbauer spectra for $A[Mn(II)Fe(III)(ox)_3]$ compounds with $A^+ = P(C_6H_5)_4^+$ (**2**), $As(C_6H_5)_4^+$ (**3**) and NPr_4^+ (**4**), in order to elucidate the effect of the kinds of the counter cation on the magnetic structure of the Mn(II)-Fe(III) system, where C_6H_5 and Pr are phenyl and *n*-propyl groups, respectively. The spin directions in mixed crystals $NPr_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ (x = 0.05 - 0.95) were also investigated by ^{57}Fe Mössbauer spectroscopy.

EXPERIMENTAL

Compounds **2-4** were prepared as microcrystals according to the procedures previously reported[10,11]. Compounds $NPr_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ (x = 0.04, 0.29, 0.45, 0.68, 0.88 and 0.93) were prepared by adding an aqueous solution (5 ml) of $MnCl_2{\cdot}4H_2O$ (1 mmol) to an aqueous solution (10 ml) containing NPr_4Br (2 mmol), $K_3Fe(ox)_3{\cdot}3H_2O$ and $K_3Cr(ox)_3{\cdot}3H_2O$ (total amount of $K_3Fe(ox)_3{\cdot}3H_2O$ and $K_3Cr(ox)_3{\cdot}3H_2O$ = 1 mmol). The microcrystals formed were collected by centrifugation, washed with water, and dried over P_4O_{10}. $K_3Fe(ox)_3{\cdot}3H_2O$ samples enriched to 48.8 and 8.1 % in ^{57}Fe were employed for the preparations of the compounds with x = 0.04 and 0.29, respectively. The chemical compositions were determined from the ICP data for Cr, the atomic absorption data for Fe and Mn, and the microanalysis data for C, H and N. Mössbauer spectra were measured in the temperature range of 4.2 – 298 K with an instrument described previously[4]. The isomer shifts are reported relative to metallic iron foil. XRD measurements were carried out for compounds **2-4** to calculate the distances between the basal layers (d) from the hexagonal cell parameter c_0[12]. The d value obtained for each compound was essentially consistent with that reported in the literature[11].

RESULTS AND DISCUSSION

All the compounds **2-** exhibited a magneticall relaxed or split Mössbaue spectrum below the Né temperature (T_N = 25–2 K[11]). The Mössbaue spectra at 4.2 K of th compounds **2-4** consiste of a well-resolved sext showing an axi symmetry around the ^{57}F nucleus, as shown i Figure 1. The angle (Θ between the intern magnetic field ($\boldsymbol{H}_n$) an the principal axis of V_{zz} the Mössbauer nucleus i each of the thre compounds was estimate at 4.2 K by applying th following approximat equation for axi symmetry; S_1 – S = -1/2$eV_{zz}Q$(3cos$^2\Theta$ – 1), where S_1 and S_2 represent the interval between the lowest-energy and the second lowest-energy peaks, and that between

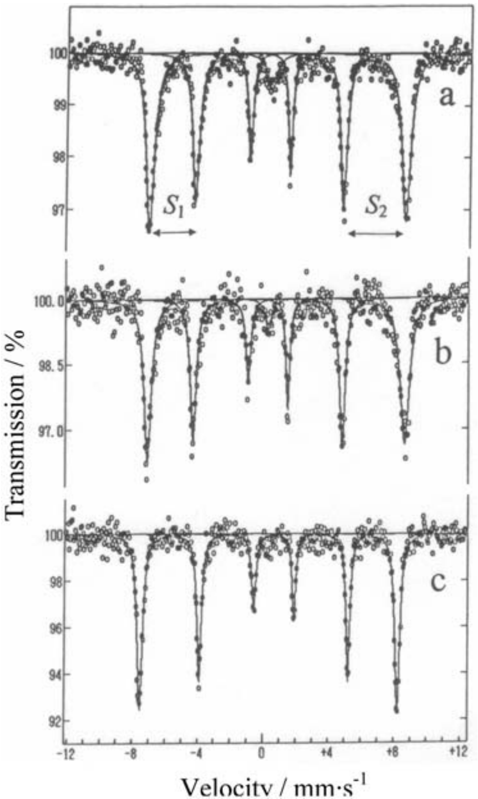

FIGURE 1 ^{57}Fe Mössbauer spectra at 4.2 K of (a) compound **2**, (b) compound **3** and (c) compound **4**.

TABLE 1 The magnitude of internal field (H_n), the Θ angle and the distance between the basal layers (d) estimated for compounds **1-4**

Compound	**1**	**2**	**3**	**4**
H_n/kOe	502 [a)]	489	493	493
Θ /°	52 [a)]	21	20	83
d /Å	8.95	9.52	9.65	8.20

a) References 4 and 7.

the highest-energy and the second highest-energy peaks, respectively[13]. The quadrupole splitting (ΔE_Q) just above T_N (0.61, 0.62 and 0.66 mm/s at 30 K for **2-4**, respectively) was employed as the value of $|1/2eV_{zz}Q|$ in the equation. The principal axis of V_{zz} of iron in both the M(II) and M'(III) sites of the A[M(II)M'(III)(ox)$_3$] compounds with spherical A^+ is rationally thought to coincide with the D_3 axis which goes through the iron atoms and is perpendicular to the basal layers[2,6].

Compounds **2** and **3** having larger values of the distance between the basal layers (d = 9.52 and 9.65 Å, respectively) than that of **1** (d = 8.95 Å) exhibited Mössbauer spectra noticeable for the $S_1 < S_2$ relationship, which afforded small Θ values (21° for **2** and 20° for **3**) indicating spin directions almost perpendicular to the basal layers. The positive sign of V_{zz} was determined for both compounds; the same sign was reported for NBu$_4$[M(II)Fe(III) (ox)$_3$] compounds[4,6,7]. The Θ values of **2** and **3** were different from the intermediate Θ value (52°) of **1**, and well coincided with those of NBu$_4$[Ni(II)Fe(III) (ox)$_3$][4] and ^{57}Fe(III)-doped NBu$_4$[Mn(II)Cr(III)(ox)$_3$][6]. The Mössbauer parameters obtained were listed in Table 1 along with the d value for each compound. A similar perpendicular spin alignment was also shown for P(C$_6$D$_5$)$_4$[Mn(II) Fe(III)(ox)$_3$] by a neutron diffraction study[14].

In the Mössbauer spectrum of compound **4** with the shortest d (8.20 Å), on the other hand, the S_1 was

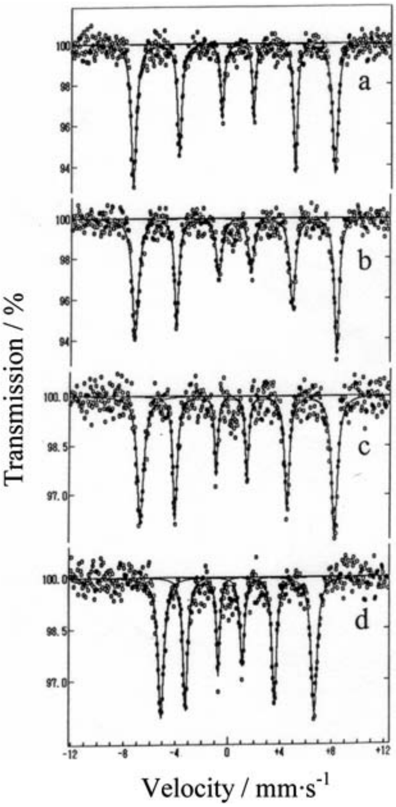

FIGURE 2 ^{57}Fe Mössbaer spectra of NPr$_4$[Mn(II)Fe(III)$_x$Cr(III)$_{1-x}$ (ox)$_3$] with x = (a) 0.93, (b) 0.88, (c) 0.68 and (d) 0.04.

observed to be fairly larger than S_2 (Figure 1b); the estimated Θ value (83°) indicates a nearly parallel direction of spin alignment ($V_{zz} > 0$, see the next paragraph). The above results reveal that the spin direction in the present Mn(II)-Fe(III) system, a combination of magnetically-isotropic ions, is very sensitive to the d value and it can be controlled by choosing the A^+ of appropriate bulkiness. Some competition between an intralayer interaction and an interlayer interaction is suggestive, although the mechanism governing the spin direction is not understood at present. To get information about the effect of A^+ in the compounds including a metal ion with single ion anisotropy, for comparison, the Θ values were estimated for $P(C_6H_5)_4[Fe(II)Cr(III)(ox)_3]$ and $P(C_6H_5)_4[M(II)Fe(III)\ (ox)_3]$ (M = Fe, Co) by the spectroscopy. All the compounds showed Θ values close to 90° in accord with the cases of the NBu_4^+ analogues[1,2,8].

$NPr_4[Mn(II)Cr(III)(ox)_3]$ (**5**) is known to exhibit a spin direction almost perpendicular to the basal layers[5,9]. Another kind of control of the spin direction could be achieved by the mixed crystallization of **4** and **5**. Selected ^{57}Fe Mössbauer spectra at 4.2 K of the mixed crystals $NPr_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ (x = 0.04 – 0.93) are shown in Figure 2. Although the $S_1 > S_2$ relationship was observed for the compound with x = 0.93 (Figure 2a), like that in $NPr_4[Mn(II)Fe(III)(ox)_3]$ (x = 1.0), the S_1 became comparable to the S_2 at x = 0.88 (Figure 2b). When x decreased below ca. 0.5, the S_1 - S_2 showed a large negative value around 1.2 mm/s (Figure 2d). The Θ value at the Fe(III) in each $NPr_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ compound of x = 0.04 – 0.68 was obtained with the positive sign of V_{zz}, by the same procedure applied to **2-4**. On the other hand, no change of the sign of the V_{zz} with changing x (from 0.04 to 1.0) was confirmed from the fact that the ΔE_Q of $NPr_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$

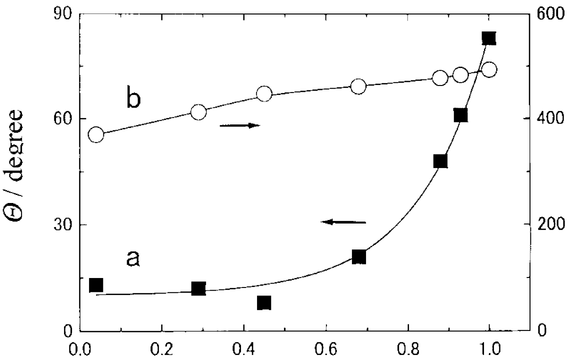

FIGURE 3 The variations of (a) Θ and (b) H_n with x for $NPr_4[Mn(II)\ Fe(III)_xCr(III)_{1-x}(ox)_3]$

is substantially constant (0.64 - 0.66 mm/s at 30 K) independently of the x value; the Θ values at $x = 0.88$ and 0.93 were also calculated on the basis of the positive sign of V_{zz}. The Θ vs. x plots in Figure 3a clearly show that the spin direction in the mixed crystal system is continuously controllable in a wide range of Θ. The Θ decreased rapidly first on lowering the x from 1.0, and then it approached a constant value close to zero ($\Theta \sim 10°$ at $x = 0.04$). The H_n values at the Fe(III) nucleus (4.2 K) were plotted against x in Figure 3b, indicating a lower H_n for a smaller x. Variable-temperature Mössbauer measurements revealed that the T_N of $NPr_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ decreases on lowering x (T_N = ca. 10 and 25 K for $x = 0.04$ and 0.95, respectively), which would be responsible for the $\Theta - x$ profile in Figure 3b.

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