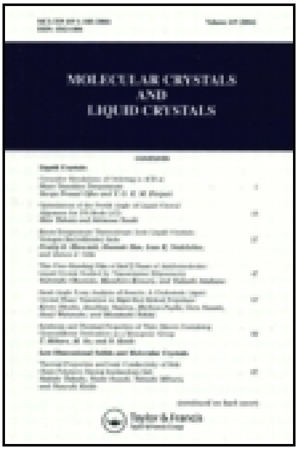

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Mössbauer Study of Molecule-Based Magnets: $NBu_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ and Related Compounds

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The internal magnetic field ($\boldsymbol{H}_n$) at ^{57}Fe nucleus was investigated for the mixed crystals $NBu_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ ($x = 0.04 - 1.0$) by using Mössbauer spectroscopy, where NBu_4^+ = tetra(*n*-butyl)ammonium ion and ox^{2-} = oxalate ion. The angle (Θ) between $\boldsymbol{H}_n$ and the principal axis of V_{ZZ} was observed to change from ~50° to ~10° with the decrease of the x value (V_{ZZ} = the principal component of the electric field gradient tensor); the plot of Θ against x indicates that the Cr(III) spins in $NBu_4[Mn(II)Cr(III)(ox)_3]$ are aligned along an axis almost perpendicular to the honeycomb layers consisting of an alternate array of Mn(II) and Cr(III) ions through ox^{2-} ligands. The Θ values estimated for the ^{57}Fe nuclei in the bivalent and tervalent sites of $NBu_4[Fe(II)_{0.03}Mn(II)_{0.97}Fe(III)_{0.02}Cr(III)_{0.98}(ox)_3]$ were similar to each other.

Keywords: Mössbauer spectroscopy; oxalates; spin direction

INTRODUCTION

In the field of molecule-based magnetism, oxalate-bridged mixed-metal assemblies $A[M(II)M'(III)(ox)_3]$ have attracted particular interest [1-3], where A^+ = organic cations such as quarternary ammonium ions and ox^{2-} = oxalate ion. 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^+ [4]. For the investigation of the electronic and magnetic structures of the $A[M(II)M'(III)(ox)_3]$ compounds containing iron atoms, ^{57}Fe Mössbauer spectroscopy has been employed as a powerful tool [5-9]. The angle (Θ) between the internal magnetic field ($\boldsymbol{H}_n$) and the principal axis of V_{zz} at the Mössbauer nucleus can be obtained from the spectra of a magnet [10,11], where V_{zz} is the principal component of the electric field gradient tensor and $0° \leq \Theta \leq 90°$. The principal axis of V_{zz} of iron in both the M(II) and M'(III) sites of $A[M (II)M'(III)(ox)_3]$ is rationally thought to coincide with the D_3 axis which goes through the iron atoms and is perpendicular to the basal layers [6,8]. The previous paper [9] reported a variation of the Θ at the Fe(III) in the mixed crystal system $NBu_4[Fe(II)_x\ Mn(II)_{1-x}Cr(III)(ox)_3]$ (NBu_4^+ = tetra(*n*-butyl)ammonium ion). In the present study, we have measured ^{57}Fe Mössbauer spectra for $NBu_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ (NBu_4^+ = tetra(*n*-butyl)ammonium ion) from the interest in the spin direction at the tervalent metal site. The Θ values at the divalent and tervalent sites were compared each other in an identical compound $NBu_4[Fe(II)_{0.03}\ Mn(II)_{0.97}Fe(III)_{0.02}Cr(III)_{0.98}(ox)_3]$.

EXPERIMENTAL

Compounds $NBu_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ (x = 0.04, 0.26, 0.46, 0.71, 0.86 and 0.96) were prepared by adding an aqueous solution (3 ml) of $MnCl_2\cdot 4H_2O$ (2 mmol) to an aqueous solution (10 ml) containing NBu_4Br (3 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 $K_3Cr(ox)_3\cdot 3H_2O$ = 2 mmol). The microcrystals formed were collected by filter suction, washed with water, and dried over P_4O_{10}. Enrichments of ^{57}Fe were made for the cases x = 0.04 and 0.26; the isotopic abundances of ^{57}Fe were calculated to be 48.8 and 9.96 %, respectively. Compound $NBu_4[Fe(II)_{0.03}Mn(II)_{0.97}Fe(III)_{0.02}Cr(III)_{0.98}(ox)_3]$ was prepared by adding an aqueous solution (3 ml) containing $^{57}FeSO_4 \cdot 7H_2O$ (0.06 mmol, isotopic abundance of ^{57}Fe = 95.3 %) and $MnCl_2 \cdot 4H_2O$ (1.94 mmol) to an aqueous solution (10 ml) containing $K_3Fe(ox)_3 \cdot 3H_2O$ (0.06 mmol), $K_3Cr(ox)_3 \cdot 3H_2O$ (1.94 mmol) and NBu_4Br (3 mmol). 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 with an instrument described previously [8]. The isomer shifts are reported relative to metallic iron foil.

RESULTS AND DISCUSSION

Compound $NBu_4[Mn(II)Fe(III)(ox)_3]$ is reported to act as an antiferromagnet with spin canting below the critical temperature, T_C = 28 K [2,3], and on the other hand, $NBu_4[Mn(II)Cr(III)(ox)_3]$ is known to be a ferromagnet with T_C = 6 K [1]. The Mössbauer spectra of $NBu_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ with x = 0.04, 0.26, 0.46, 0.71 and 0.96 measured at 4.2 K are shown in Fig. 1; a well-resolved sextet was seen in each spectrum. A significant variation of the $S_1 - S_2$ value with x was observed in the spectra of $NBu_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$, where S_1 and S_2 represent the interval between the lowest-energy and the second lowest-energy peaks, and that between the highest-energy and the second highest-energy peaks in a Zeeman split Mössbauer sextet. The S_2 was comparable to the S_1 at 4.2 K in the compound with x = 0.96 (Fig. 1a, $S_1 - S_2 = -0.28$ mm/s), like that in $NBu_4[Mn(II)Fe(III)(ox)_3]$ [8]. The difference between S_1 and S_2 became appreciably on lowering the x (Figs. 1b), and the $S_1 - S_2$ exhibited a large negative value (around −1.2 mm/s) at x values below ca. 0.5 (Figs. 1c-e).

For axial symmetry, the following equation can be applied on the assumption that the magnetic hyperfine interaction is much larger than the quadrupole interaction [11]; $S_1 - S_2 = (-1/2)eV_{zz}Q(3\cos^2\Theta - 1)$. The Θ value at the Fe(III) in each $NBu_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ compound of x =0.04 - 0.86 was obtained with the positive sign of V_{zz}, by employing the quadrupole splitting (ΔE_Q) just above T_c as the value of $|(1/2)eV_{zz}Q|$ for the calculation. On the other hand, no change of the sign of the V_{zz} with changing x (from 0.04 to 1) was confirmed from the fact that the ΔE_Q of $NBu_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ is almost constant independently of the x value; the Θ values at $x = 0.96$ and 1.0 were also calculated on the basis of the positive sign of V_{zz}.

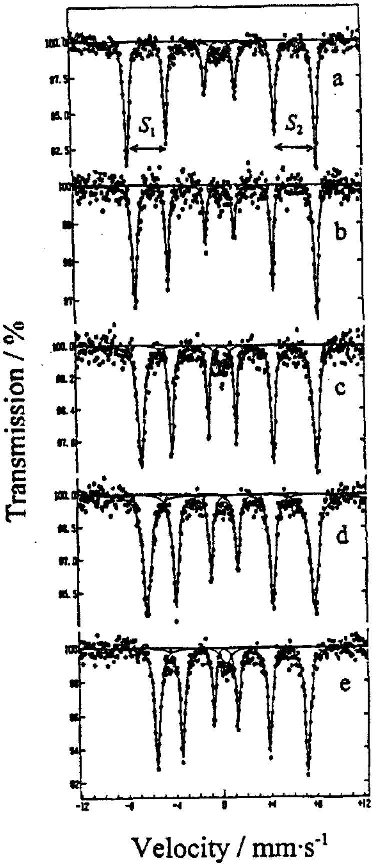

FIGURE 1 Mössbauer spectra at 4.2 K of $NBu_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ with x = (a) 0.96, (b) 0.71, (c) 0.46, (d) 0.26 and (e) 0.04.

It was clearly shown in the Θ vs. x plots (Fig. 2a) that the Θ decreased rapidly first on lowering the x from 1.0, and then it approached a constant value close to zero (Θ ~ 10° at x = 0.04). Fig. 2a evidences that the Cr(III) spins in NBu$_4$[Mn(II)Cr(III)(ox)$_3$] (x = 0) are aligned along an axis almost perpendicular to the basal planes consisting of the alternate array of the M(II) and M(III)' ions through ox^{2-} ligands; the direction of Fe(III) spin shows the direction of spin alignment in the pure Cr(III) sublattice at extremely small x values. Our previous work on NBu$_4$[Fe(II)$_x$Mn(II)$_{1-x}$Cr(III)(ox)$_3$] [9] concluded that the direction of Mn(II) spins in NBu$_4$[Mn(II)Cr(III)(ox)$_3$] is also approximately perpendicular to the basal planes. However, the Θ - x profile for the Fe(II) of NBu$_4$[Fe(II)$_x$Mn(II)$_{1-x}$Cr(III)(ox)$_3$] (Fig. 2b) is fairly different from that for the Fe(III) of NBu$_4$[Mn(II)Fe(III)$_x$Cr(III)$_{1-x}$(ox)$_3$]

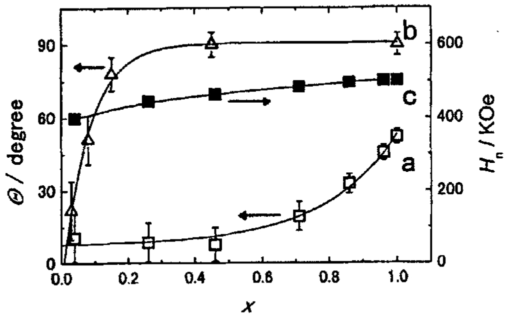

FIGURE 2 The variations of Θ with x for (a) NBu$_4$[Mn(II)Fe(III)$_x$Cr(III)$_{1-x}$(ox)$_3$] and (b) NBu$_4$[Fe(II)$_x$Mn(II)$_{1-x}$Cr(III)(ox)$_3$] [9], and (c) the variation of H_n with x for NBu$_4$[Mn(II)Fe(III)$_x$Cr(III)$_{1-x}$(ox)$_3$].

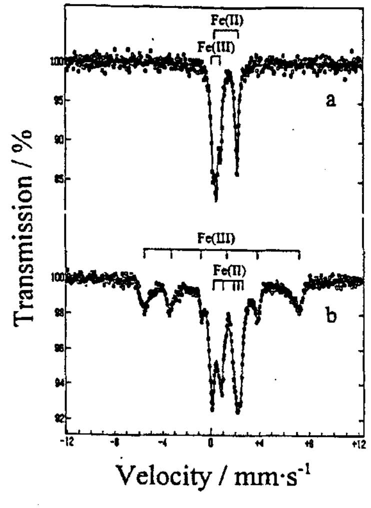

FIGURE 3 Mössbauer spectra of NBu$_4$[Fe(II)$_{0.03}$Mn(II)$_{0.97}$Fe(III)$_{0.02}$Cr(III)$_{0.98}$(ox)$_3$] at (a) 20 K and (b) 4.2 K.

(Fig. 2a). In the former case, the single ion anisotropy of high-spin Fe(II) is ascribable to the Θ - x profile [9]. The values of internal magnetic field (H_n) at Fe(III) estimated for $NBu_4[Mn(II)Fe(III)_xCr(III)_{1-x}(ox)_3]$ (4.2 K) were plotted against x in Fig. 2c.

The Mössbauer spectra of $NBu_4[Fe(II)_{0.03}Mn(II)_{0.97}Fe(III)_{0.02}Cr(III)_{0.98}(ox)_3]$ are shown in Fig. 3. At 4.2 K, this compound exhibited a superimposed spectrum of magnetically split Fe(II) and Fe(III) absorptions (Fig. 3b). The Θ values at ^{57}Fe nuclei in the bivalent and tervalent sites were estimated to be 28 ± 12° [5,10] and 21 ± 8°, respectively. This result suggests that Mn(II) and Cr(III) spins are almost parallel each other in this compound.

References

[1] H. Tamaki, Z. J. Zhong, N. Matsumoto, S. Kida, M. Koikawa, N. Achiwa, Y. Hashimoto and H. Okawa, *J. Am. Chem. Soc.*, **114,** 6974 (1992).

[2] H. Tamaki, M. Mitsumi, K. Nakamura, N. Matsumoto, S. Kida, H. Okawa and S. Iijima, *Chem. Lett.*, 1975 (1992).

[3] C. Mathonière, C. J. Nuttall, S. G. Carling and P. Day, *Inorg. Chem.*, **35,** 1201 (1996).

[4] R. Pellaux, H. W. Schmalle, R. Huber, P. Fisher, T. Hauss, B. Ouladdiaf and S. Decurtins *Inorg. Chem.*, **36**, 2301 (1997), and references quoted therein.

[5] S. Iijima, T. Katsura, H. Tamaki, M. Mitsumi, N. Matsumoto and H. Okawa, *Mol. Cryst. Liq. Cryst.*, **233,** 263 (1993).

[6] N. S. Ovanesyan, G. V. Shilov, L. O. Atovmyan, R. N. Lyubovskaya, A. A. Pyalling and Yu. G. Morozov, *Mol. Cryst. Liq. Cryst.*, **273,** 175 (1995).

[7] W. M. Reiff, J. Kreisz, L. Meda and R. U. Kirss, *Mol. Cryst. Liq. Cryst.*, **273,** 181 (1995).

[8] S. Iijima, F. Mizutani, M. Mitsumi, N. Matsumoto and H. Okawa, *Inorg. Chim. Acta*, **253,** 47 (1996).

[9] S. Iijima, S. Koner and F. Mizutani, *J. Radioanal. Nucl. Chem.*, **239,** 245 (1999).

[10] S. V. Karyagin, *Sov. Phys. Solid State*, **8,** 391 (1966).

[11] W. M. Reiff, *Coord. Chem. Rev.*, **10,** 37 (1973).