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MOESSBAUER SPECTROSCOPIC STUDY OF MAGNETIC ORDERING IN OXALATE-BRIDGED Cr(III)-Fe(II) AND Fe(III)-Fe(II) SYSTEMS

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Abstract Magnetic ordering phenomena in mixed-metal assemblies $\{NBu_4[Fe(II)M(III)(ox)_3]\}_{3\infty}$ (M=Cr (1), Fe (2)) were studied by using ^{57}Fe Moessbauer spectroscopy, where NBu_4^+=tetra(*n*-butyl)ammonium ion, ox^{2-}=oxalate ion. Nuclear Zeeman splittings were observed in the Moessbauer spectra of both 1 and 2 at low temperatures (below 10 K for 1 and 41 K for 2), which indicated the occurrence of three-dimensional magnetic ordering in these complexes under zero applied field.

INTRODUCTION

A promising strategy to obtain molecular-based magnets consists of assembling two kinds of transition metal ions through organic ligands which transmit the magnetic interaction between the ions over long distances.[1-6] Ōkawa et al. have recently reported a series of metal complexes with the formula of $\{NBu_4[M'(II)M(III)(ox)_3]\}_{3\infty}$ (NBu_4^+=tetra(*n*-butyl)ammonium ion, ox^{2-}=oxalate ion), and revealed that some of them exhibit bulk magnetic behavior at low temperatures by using cryomagnetic measurements.[4-6] The oxalate-bridged complexes were designed to have an isotropic three-dimensional assembly of alternately arrayed M(III) and M'(II) ions, as shown in Figure 1. It was reported that the ferromagnetic interaction between Cr(III) and M'(II) (M'=Mn, Fe, Co, Ni, Cu) yielded ferromagnets,[4,5] and that Fe(III) coupled with M'(II) (M'=Fe, Ni) antiferromagnetically led to ferrimagnets.[6] Moessbauer spectroscopy is well known to be a powerful tool for investigating magnetic materials, especially in the case where the material contains iron atoms. In the present work, we have meas-

ured ^{57}Fe Moessbauer spectra for $\{NBu_4[FeCr(ox)_3]\}_{3\infty}$ (1) and $\{NBu_4[FeFe(ox)_3]\}_{3\infty}$ (2) in order to get further information about the magnetic ordering phenomena in these oxalate-bridged systems.

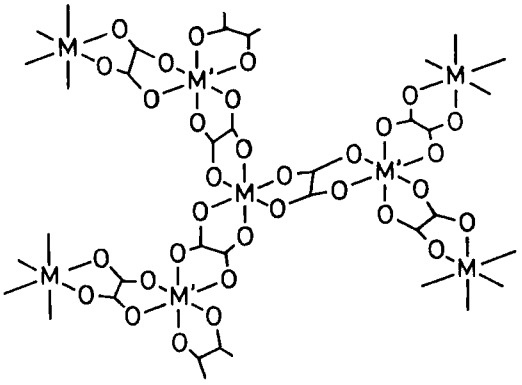

FIGURE 1 Possible three-dimensional network structure of $\{NBu_4[M'(II)M(III)(ox)_3]\}_{3\infty}$

EXPERIMENTAL

Compound 1 was obtained as microcrystals by the reaction of $K_3[Cr(ox)_3]\cdot 3H_2O$ with $FeSO_4\cdot 7H_2O$ in water, in the presence of tetra-*n*-butylammonium bromide.[5] Compound 2 was prepared similarly by using $K_3[Fe(ox)_3]\cdot 3H_2O$ in place of $K_3[Cr(ox)_3]\cdot 3H_2O$.[6]

As the radio active source for Moessbauer measurements, a $^{57}Co(Rh)$ moving in a constant acceleration mode was used. The Moessbauer spectra were obtained by using a Wissel 1200 spectrometer and a proportional counter. The hyperfine parameters were obtained by least-squares fitting to Lorentzian peaks. The isomer shifts are reported relative to metallic iron foil. For the paramagnetic states, the quadrupole splitting represents only the peak separation of quadrupole doublet, because the sign of quadrupole splitting can not be determined in these cases. The sample temperature was controlled by a Heli-tran liquid transfer refrigerator (Air Products and Chemicals, Inc.) with the accuracy of ±0.5 K.

RESULTS AND DISCUSSION

The ^{57}Fe Moessbauer spectra measured for 1 at 298, 78, 12, 10 and 4.2 K are shown in Figure 2. The isomer shift (δ) and the quadrupole

splitting (ΔE_Q) at each temperature are summarized in Table I along with the other parameters mentioned below. It was shown that 1 orders ferromagnetically at T_c = 12 K by the temperature dependence of its magnetization measured in a weak magnetic field.[5] Above this temperature, the Moessbauer spectra of 1 consisted of a single quadrupole doublet showing the ordinary paramagnetism of Fe(II), where the electron spin of Fe(II) fluctuated rapidly so as to yield zero time-averaged field at the iron nucleus. The large δ (1.32 mm/s at 78 K) and the strong temperature dependence of ΔE_Q at higher temperatures (ΔE_Q = 1.82 mm/s at 78 K and 1.26 mm/s at 298 K) suggested a high-spin state (S = 2) of Fe(II).[7,8]

When the temperature was lowered below 12 K, the shape of the spectrum changed to give apparently a doublet at the lower energy side and a triplet at the higher energy side with small splits, which

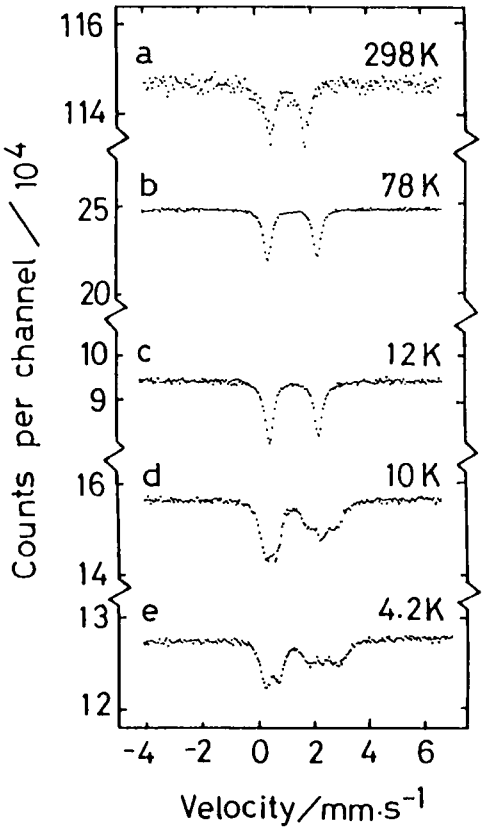

FIGURE 2 Moessbauer spectra of Compound 1.

is characteristic of ^{57}Fe Moessbauer spectrum with negative ΔE_Q and small nuclear Zeeman splittings.[9,10] The rapid development of nuclear Zeeman splittings[11] between 12 and 10 K clearly indicates the occurrence of three-dimensional magnetic ordering in 1. The spectra at 10 and 4.2 K were analyzed by using the hyperfine parameters δ, ΔE_Q, H_n and Θ (Table I), with the ordinary procedure for the cases where the magnetic hyperfine interaction is smaller than the quadrupole interaction.[9,12,13] Here, H_n and Θ represent the magnitude of the internal magnetic field at ^{57}Fe nucleus and the angle between the internal magnetic field and the principal axis of V_{zz} (the principal component of the electric field gradient tensor), respectively. Axial symmetry was assumed for the array of the ligands around Fe(II) in the analysis.

The observed H_n (38 kOe at 4.2 K) was exceptionally small, although a wide variety of H_n were reported for high-spin Fe(II) in different chemical environments.[8] H_n can be divided into three components, the Fermi contact term (H_S), the orbital moment contribution (H_L) and the dipolar interaction (H_D).[8,10,11] Usually, H_S predominantly contributes to H_n. Mixed-metal assembly 1 would be a system where H_L is fairly large and opposes H_S, similarly to the case of anhydrous $FeCl_2$.[8] In addition, delocalization effects of oxalate ligand may contribute in some extent to decreasing H_n.[11]

The Moessbauer spectra measured for 2 at 78, 45, 41, 35 and 4.2

TABLE I Hyperfine parameters for Compound 1.

Temperature/K	δ [a]/mm·s^{-1}	ΔE_Q/mm·s^{-1}	H_n/kOe	Θ
298	1.18	1.26[b]		
78	1.32	1.82[b]		
12	1.33	1.82[b]		
10	1.32	-1.85	35	90°
4.2	1.33	-1.86	38	90°

a) Isomer shift relative to metallic iron at 298 K.
b) Quadrupole splitting in the paramagnetic state represents only the distance of the splitting in the Moessbauer spectrum due to the quadrupole inteaction.

K are shown in Figure 3. Above the temperature (43 K) reported to be the ferrimagnetic-paramagnetic transition temperature of 2 by cryomagnetic measurements,[6] four absorption lines were observed in the Moessbauer spectrum. This spectrum-shape shows the presence of two kinds of iron atoms, each of which gives a quadrupole doublet; Compound 2 is a "trapped-valence type" Fe(II)-Fe(III) system where the electron transfer rate between the two irons is less than the Moessbauer time scale (rate < 10^7 s^{-1}).[14] The absorption lines were assigned as shown in the spectrum at 78 K (Figure 3a). This assignment afforded hyperfine parameters (δ = 1.30 mm/s and ΔE_Q = 1.79 mm/s) which are similar to those of Fe(II) in 1 at the same temperature, to the Fe(II) in 2. On the other hand, δ and ΔE_Q were obtained to be 0.51 and 0.60 mm/s, respectively, for the Fe(III).

At 41 K, the spectrum began to show a complicated shape (Figure 3c). The centered absorption lines somewhat broadened and the base line was winding apparently. As the temperature was further low-

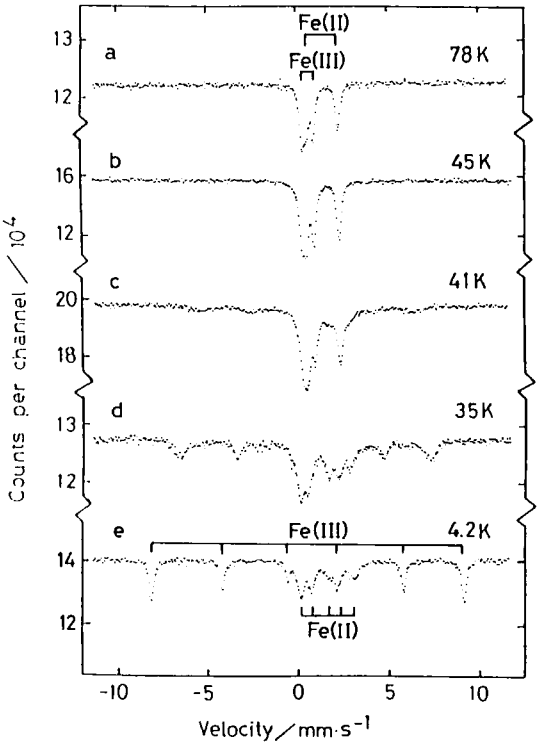

FIGURE 3 Moessbauer spectra of Compound 2.

ered, the spectrum showed a number of absorption lines spreading over a wide energy range. The spectra below 41 K can be understood as a superposition of the absorptions of Fe(II) and Fe(III) split magnetically, as shown in Figure 3e. The line component of Fe(II) was very similar to the spectrum of 1 observed below T_C: hyperfine parameters δ, ΔE_Q, H_n and Θ were estimated as 1.32 mm/s, -1.92 mm/s, 52 kOe and 90°, respectively, for the Fe(II) at 4.2 K, by using the same procedure applied to 1. On the other hand, the line component of Fe(III) can be analyzed as a case where the magnetic hyperfine interaction is much larger than the quadrupole interaction.[11] H_n was estimated to be 537 kOe at 4.2 K, and this value is typical for high spin Fe(III).[11]

The above results obtained by Moessbauer spectroscopy give strong evidence for the three-dimensional magnetic ordering in mixed-metal assemblies $\{NBu_4[M'(II)M(III)(ox)_3]\}_{3\infty}$ under zero applied field, and are essentially consistent with the results of previous cryomagnetic measurements.[4-6]

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