

Spin-glass behavior and magnetic splitting in molecular magnetic materials $\{[N(n-C_4H_9)_4][M^{II}Fe^{III}(C_2O_4)_3]\}_n$ ($M = Co, Mn$)

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Abstract The mixed valence character and the antiferromagnetic coupling in the molecular magnetic materials $\{[N(n-C_4H_9)_4][M^{II}Fe^{III}(C_2O_4)_3]\}_n$ ($M = Co, Mn$) were investigated by Mössbauer spectroscopy and magnetic measurements. In the material $\{[N(n-C_4H_9)_4][CoFe(C_2O_4)_3]\}_n$, the appearance of the spin-glass phase transition temperature and the magnetic phase transition under zero-field-cooled AC magnetic measurements were studied in the temperature range 5–100 K. In the Mössbauer spectra of $\{[N(n-C_4H_9)_4][MnFe(C_2O_4)_3]\}$ a magnetic splitting was observed below 30 K. The appearance of the magnetic splitting indicates the occurrence of magnetic ordering in this complex. The hyperfine parameters show that the electronic state of iron is high-spin Fe^{3+} .

Keywords Oxalate bridging · Molecule-based magnet · Spin-glass behavior · Magnetic splitting · Mössbauer

1 Introduction

Molecular magnets have been the subject of studies of polymer chemistry synthesis of magnetic materials at low temperatures [1–4]. The design and synthesis of molecular magnets has become a hot topic at the forefront of physics, chemistry, materials and life sciences and many other areas. Oxalate bridged ligands have good magnetic interaction capacity between metal ions and oxalate bridged molecular magnets play an important role due to their special structure and outstanding magnetic properties

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in the magnetic field [5–9]. In this paper, molecular magnetic materials $\{[N(n-C_4H_9)_4][M^{II}Fe^{III}(C_2O_4)_3]\}_n$ ($M = Co, Mn$) were selected and have been studied through elemental analysis, IR, Mossbauer spectroscopy, magnetic measurements, etc. We report a detailed investigation of their spin-glass and magnetic splitting behavior.

2 Experiment section

2.1 Materials and physical measurements

Commercially obtained starting materials were used. $K_3[Fe(C_2O_4)_3]$ was prepared according to literature methods. NBu_4Br , $CoCl_2 \cdot 6H_2O$ and $FeCl_2$ are reagent grade, without further purification. Powder X-ray diffraction patterns were measured with a Rigaku RINT 2100 instrument ($Cu-K\alpha$). Magnetic measurements were made using a Quantum Design MPMS 7 SQUID magnetometer working in both the cooling and warming modes. The radioactive source used for Mössbauer measurements was ^{57}Co (Pd). The absorption Mössbauer spectra were recorded using a conventional constant acceleration spectrometer. All Mössbauer spectra were fitted with the MössWin3.0 software.

2.2 Synthesis

The compound $\{[N(n-C_4H_9)_4][CoFe(C_2O_4)_3]\}_n$ was prepared by the following method: An aqueous solution of $K_3[Fe(C_2O_4)_3]$ (2.0 mmol) was added to an aqueous solution of $CoCl_2 \cdot 6H_2O$ (2.0 mmol) under Ar atmosphere in the dark at room temperature. After 30 min, the solution was filtered to remove the remaining small amount of $Fe(C_2O_4)$. The precipitate was dialyzed by adding a methanol solution of NBu_4Br (2.2 mmol) to the filtrate. Thereafter the resulting green precipitate was washed with distilled water and dried. Analysis for $C_{22}H_{36}NO_{12}FeCo$. calculated : C, 42.53; H, 5.84; N, 2.25. Found: C, 42.81; H, 5.27; N, 2.32.

The compound $\{[N(n-C_4H_9)_4][MnFe(C_2O_4)_3]\}_n$ was prepared by the following method: An aqueous solution of $K_3[Fe(C_2O_4)_3]$ (2.0 mmol) was added to an aqueous solution of $MnSO_4 \cdot 4H_2O$ (2.0 mmol) under Ar atmosphere in the dark at room temperature. After 30 min, the solution was filtered to remove the remaining small amount of $Fe(C_2O_4)$. The precipitate was dialyzed by adding a methanol solution of $N(C_4H_9)_4Br$ (2.2 mmol) to the filtrate. Thereafter the resulting green precipitate was washed with distilled water and dried. Analysis for $C_{22}H_{36}NO_{12}FeMn$. calculated : C, 42.81; H, 5.88; N, 2.27. Found: C, 42.6; H, 6.02; N, 2.12.

3 Results and discussion

3.1 Characterization

Infrared analysis, thermogravimetric analysis, elemental analysis and ICP-AES were used to characterize the samples. The FT-IR spectrum of $\{[N(n-C_4H_9)_4][Co^{II}Fe^{III}(C_2O_4)_3]\}_n$ is shown in Fig. 1. The figure shows C_2O_4 stretching

Fig. 1 FT-IR spectrum of $\{[N(n-C_4H_9)_4][CoFe(C_2O_4)_3]\}_n$

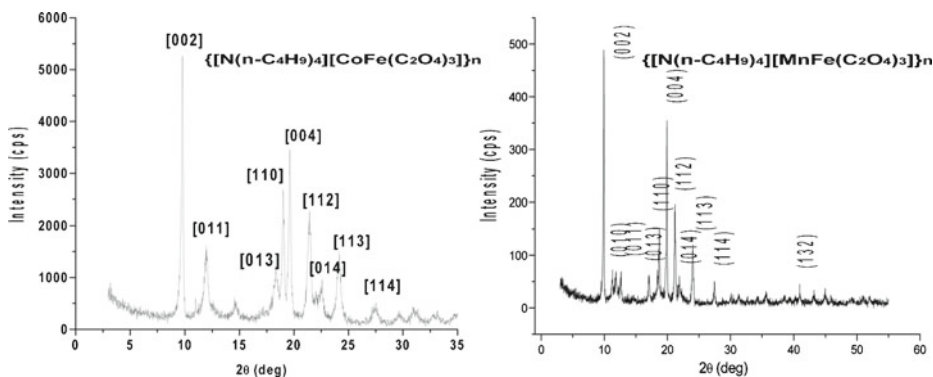
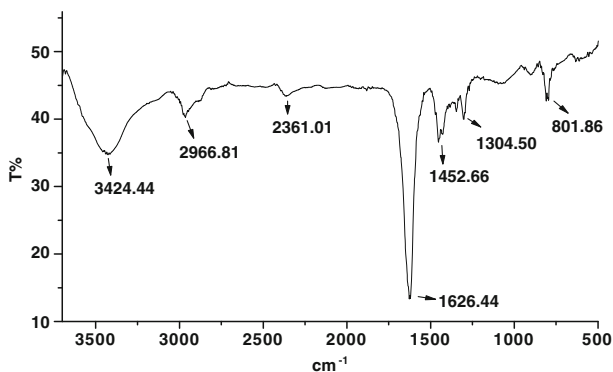


Fig. 2 XRD patterns of $\{[N(n-C_4H_9)_4][M^{II}Fe^{III}(C_2O_4)_3]\}_n$ ($M = Co, Mn$)

bands at $1,626.44\text{ cm}^{-1}$, $1,452.66\text{ cm}^{-1}$, $1,317.33\text{ cm}^{-1}$ and 801.86 cm^{-1} . The broad peak at $3,424.44\text{ cm}^{-1}$ corresponds to the $\nu(O-H)$ of the crystal water.

Figure 2 displays the XRD patterns of $\{[N(n-C_4H_9)_4][CoFe(C_2O_4)_3]\}_n$. The unit cell constants were refined on a hexagonal cell. The space group is P_{63}/mmc . The structure parameters determined from the refinement are $a = 9.49\text{ \AA}$ and $c = 17.83\text{ \AA}$. These values agree approximately with the former result reported by Mathonière et al. [3]. Figure 2 displays the XRD patterns of $\{[N(n-C_4H_9)_4][MnFe(C_2O_4)_3]\}_n$. The unit cell constants were refined on a hexagonal cell. The space group is F_{m3m} , $a = 9.39\text{ \AA}$ and $c = 53.67\text{ \AA}$.

3.2 Magnetic measurements

Measurements of the ac magnetization confirm that there exists a spin-glass behavior in the compound. The ac magnetic susceptibility of the compound was measured at 2.5 Oe ac amplitude with zero applied dc field in the frequency (f) range from 1 to 100 Hz, as shown in Fig. 3. We observed the temperature point of the spin-glass phase transition and the magnetic phase transition. It could be observed that the in-phase (real or dispersive) susceptibility, χ' (T) curves exhibited a peak at about 9 K and the peak temperature $T_f(w)$ shifted towards higher temperatures with increasing

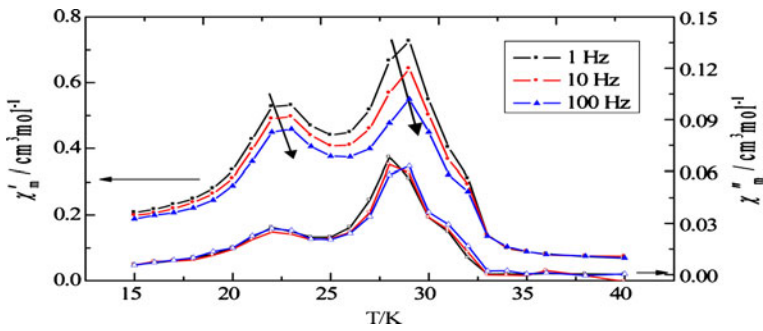


Fig. 3 ac susceptibility curve of $[[N(n-C_4H_9)_4][CoFe(C_2O_4)_3]]_n$ at $H_{ac} = 2.5$ Oe

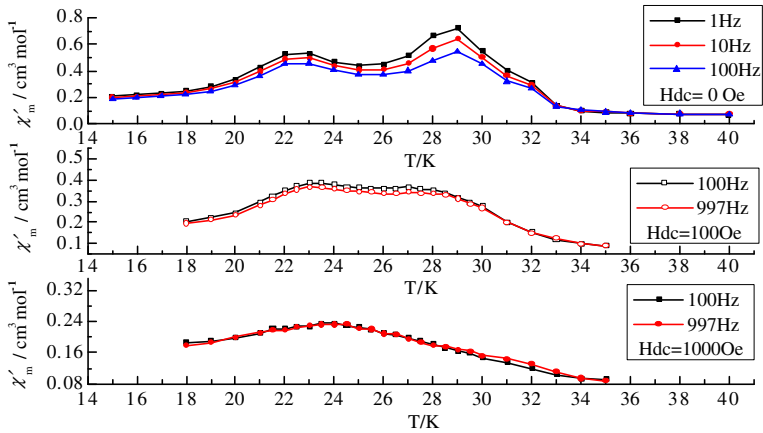


Fig. 4 ac susceptibility curve of $[[N(n-C_4H_9)_4][CoFe(C_2O_4)_3]]_n$ at different frequencies ($H_{ac} = 0$ Oe)

frequency. That the $\chi'(T)$ clearly shows a frequency dependence is typically assigned to spin glasses [10, 11].

In addition, at $H_{ac} = 2.5$ Oe, χ'' shows a broad peak at 28 K, but the out-of-phase (imaginary or absorptive) susceptibility, $\chi'(T)$, shows two clear peaks, at 22 K and 29 K respectively, and the peak temperature shifts towards higher temperatures with increasing frequency. This phenomenon indicates the coexistence of the spin glass phase and a ferrimagnetic ordered phase at low temperatures in this system [12–14].

At $H_{ac} = 2.5$ Oe, a broad peak in $\chi'(T)$ curves can be observed at about 22 K and 29 K as shown in Fig. 4. The peak temperature $T_f(w)$ shifts toward higher temperatures with increasing frequency but the bulk susceptibility is relatively decreasing, typical of spin glass behavior. The freezing temperature (T_f) is defined by the maximum in the $\chi_{ac}(T)$ plot at low frequency, here 1 Hz. The proportional relationship between the freezing temperature T_f and the logarithm of the frequency in spin-glass systems (as shown in Fig. 4) can be described by quantifying the frequency dependence through the ratio c , which may be written as $c = \frac{\Delta T_f}{T_f \Delta \log w}$. The value of c obtained for the sample is $c = 0.0217$, which falls within the range typical for conventional spin-glass systems (10^{-2} – 10^{-3}).

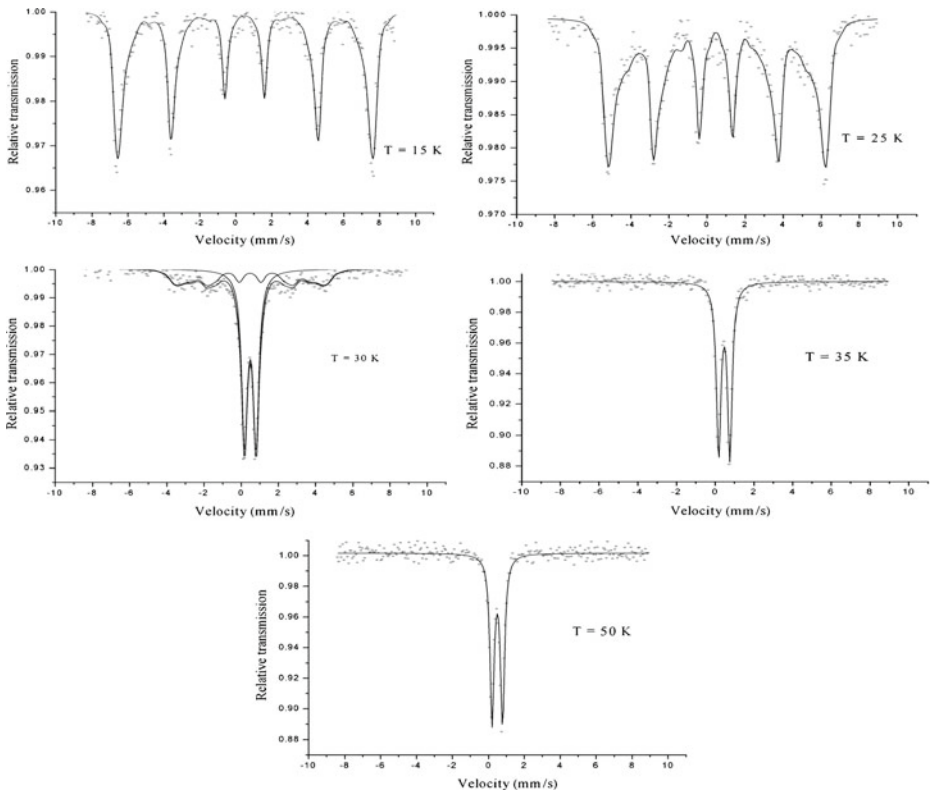


Fig. 5 Mössbauer spectra of the sample at various temperature

Table 1 Mössbauer parameters of $\{[N(n-C_4H_9)_4][FeFe(C_2O_4)_3]\}_n$ at various temperatures

Temp (K)	Doublet				Sextet				
	IS (mm/s)	QS (mm/s)	Γ (mm/s)	Area (%)	IS (mm/s)	QS (mm/s)	H_{hf} (T)	Γ (mm/s)	Area (%)
50	0.49	0.58	0.27	100					
35	0.47	0.58	0.28	100					
30	0.48	0.62	0.37	64.4	0.49	0.04	22.84	0.44	35.6
25					0.50	0.05	31.26	0.28	100
15					0.51	0.03	41.90	0.32	100

The isomer shift (IS) values relative to α -Fe at room temperature (+0.02 mm/s). QS, quadrupole splitting; Temp., temperature

3.3 Mössbauer Spectroscopy

Mössbauer spectra of $\{[N(n-C_4H_9)_4][MnFe(ox)_3]\}_n$ have been measured as a function of temperature (as shown in Fig. 5). The values of the isomer shift (IS), quadrupole splitting (QS) and hyperfine magnetic field (H_{hf}) are listed in Table 1.

Magnetic splitting is observed in the Mössbauer spectra up to 30 K (Fig. 5). The appearance of magnetic splitting indicates the occurrence of magnetic ordering in the complex. The hyperfine parameters show that the electronic state of iron is high-spin Fe^{3+} [15–17].

4 Conclusion

We have reported a detailed investigation of the magnetic properties of the molecular magnet material $\{[\text{N}(\text{n-C}_4\text{H}_9)_4][\text{M}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_n$ ($\text{M} = \text{Co}, \text{Mn}$). In the complex $\{[\text{N}(\text{n-C}_4\text{H}_9)_4][\text{Co}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}_n$ we measured the temperature of the spin-glass phase transition and the magnetic phase transition. We quantified the frequency dependence of the freezing temperature through the ratio c which is found to have the value $c = 0.0217$. Magnetic splitting was observed in the Mössbauer spectra of $\{[\text{N}(\text{n-C}_4\text{H}_9)_4][\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]\}$ below 30 K indicating magnetic order at these temperatures. The oxalate group has been shown to be an excellent bridging ligand in supporting the magnetic exchange interaction. The results of Mössbauer suggest the onset of spin canting in the sample.

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