

## Magnetic and Mössbauer spectra observed for mixed-metal magnets

### $\text{NBu}_4\text{Fe}_n^{\text{II}}\text{M}_A^{\text{II}}{}_{1-n}[\text{Fe}^{\text{III}}(\text{OX})_3](\text{M}_A=\text{Mn}, \text{Fe})$

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**Abstract** Mixed-metal molecular-based magnets  $\text{NBu}_4\text{Fe}_n^{\text{II}}\text{M}_A^{\text{II}}{}_{1-n}[\text{Fe}^{\text{III}}(\text{OX})_3]$  ( $\text{M}_A=\text{Mn}, \text{Fe}$ ) were investigated by magnetic and Mössbauer measurements. The magnetic susceptibility of  $\text{NBu}_4\text{Fe}_{0.07}^{\text{II}}\text{Mn}_{0.93}^{\text{II}}[\text{Fe}^{\text{III}}(\text{OX})_3]$  can be fitted to a Curie-Weiss law with a Weiss paramagnetic Curie temperature of  $\theta = -114.76$  K. The negative Weiss constant indicates an intramolecular antiferromagnetic coupling interaction between the adjacent Fe(II) and Fe(III) ions through the oxalate bridge. In the complex  $\text{NBu}_4\text{Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{OX})_3]$ , the Mössbauer results indicate that the  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  sublattices experience spontaneous magnetizations. The compound contains two different spin carriers; i.e.  $\text{Fe}^{\text{II}}(S = 2)$ ,  $\text{Fe}^{\text{III}}(S = 5/2)$ . Two magnetic sublattices are defined. The appearance of nuclear Zeeman splittings suggests that long range magnetic ordering takes place below 50 K.

**Keywords** Oxalate bridging · Molecule-based magnet · Multiple magnetic pole reversals · Mössbauer

## 1 Introduction

In recent decades, molecule-based magnets have been extensively studied because they show novel magnetic properties [1–4]. For instance metal ions, bridging ligands, client-based ligands, cation-anion, coordination of solvent molecules, and so on. But bridging ligands are very important because they control the range of the paramagnetic centre ions and the overlap of magnetic orbitals; they provide magnetic

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interaction of the electron transfer path and account for the effects of the compounds structure on the magnetic properties [5–8]. On the other hand, we reported that bimetallic oxalate  $NBu_4Fe^{II}[Fe^{III}(OX)_3]$  exhibits multiple magnetic pole inversions and two compensation temperatures [7]. Recently, an interesting inverse Jahn-Teller transition was predicted by Fishman et al. in bimetallic oxalates that exhibit magnetic compensation [9–11]. In the present paper, we applied a co-precipitation method to synthesize compounds of  $NBu_4Fe_{0.07}^{II}Mn_{0.93}^{II}[Fe^{III}(OX)_3]$  for which we observed a typical paramagnetic interaction. On the other hand, we performed  $^{57}Fe$  Mössbauer spectroscopy measurements in bimetallic oxalate  $NBu_4Fe^{II}[Fe^{III}(OX)_3]$  to investigate Jahn Teller distortion and multiple magnetic-pole reversal. Mössbauer results reveal that the magnetization of  $Fe^{II}$  sublattices increases more steeply than that of the  $Fe^{III}$  sublattices below  $T_C$ , which gives rise to multiple magnetic-pole reversals.

## 2 Experiment section

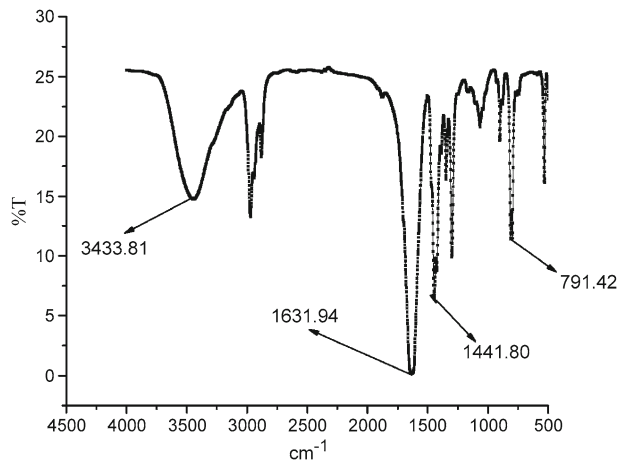
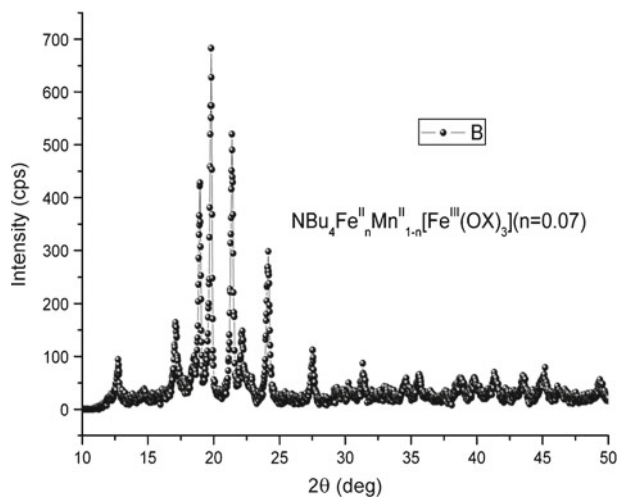
$NBu_4Br$ ,  $MnCl_2 \cdot 4H_2O$ ,  $FeSO_4 \cdot 7H_2O$  were of analytical grade from commercial source and were used without any further purification. The molecular precursor  $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$  was synthesized according to literature procedures. For the characterization of the samples we used a Perkin Elmer Corporation Spectrum One FT-IR Spectrometer Fourier transform infrared spectrometer (KBr pellet), with the radiation spectrum in the  $4000 \sim 400 \text{ cm}^{-1}$  range; a Perkin Elmer Corporation PE2400 II elemental analysis device. Magnetization measurements were measured by a Quantum Design MPMS-7S superconducting quantum interference device (SQUID) magnetometer. The powder diffraction data are measured using a Bruker D8 ADVANCE X-ray diffractometer instrument ( $Cu-K\alpha$ ).

The compound  $NBu_4Fe_{0.07}^{II}Mn_{0.93}^{II}[Fe^{III}(OX)_3]$  was prepared by the following method. To a solution of 0.0920 g (0.465 mmol)  $MnCl_2 \cdot 4H_2O$  and 0.0092 g (0.035 mmol)  $FeSO_4 \cdot 7H_2O$  in 20 ml of water, an aqueous solution of 0.2456 g (0.5 mmol)  $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$  was added dropwise. The above reaction mixture was stirred for a few minutes and then a solution of 0.2418 g (0.75 mmol)  $NBu_4Br$  in 20 ml of water was added into the mixture. After stirring for a few minutes, the reaction mixture was filtered, and the final filtrate was dried in a vacuum for one week. The compound  $NBu_4Fe^{II}[Fe^{III}(OX)_3]$  was prepared by the method described in the literature [7].

## 3 Results and discussion

### 3.1 Characterization

In Fig. 1, the IR spectra of compound  $NBu_4Fe_{0.07}^{II}Mn_{0.93}^{II}[Fe^{III}(OX)_3]$  are shown. They display the characteristic bands of the oxalate bridging ligand  $\nu_{\text{asym}(C-O)}$  at  $1631.94 \text{ cm}^{-1}$ ,  $\nu_{\text{sym}(C-O)}$  at  $1441.80 \text{ cm}^{-1}$  and  $\delta_{(O-C-O)}$  at  $791.42 \text{ cm}^{-1}$  [12]. This indicates that the oxalate ion is present as a bridging quadridentate ligand. The IR spectra of the compound exhibit a broad band near  $3433.81 \text{ cm}^{-1}$ , indicative of the

**Fig. 1** FT-IR of  $NBu_4Fe^{II}_{0.07}Mn^{II}_{0.93}[Fe^{III}(OX)_3]$ **Fig. 2** XRD of  $NBu_4Fe^{II}_{0.07}Mn^{II}_{0.93}[Fe^{III}(OX)_3]$ 

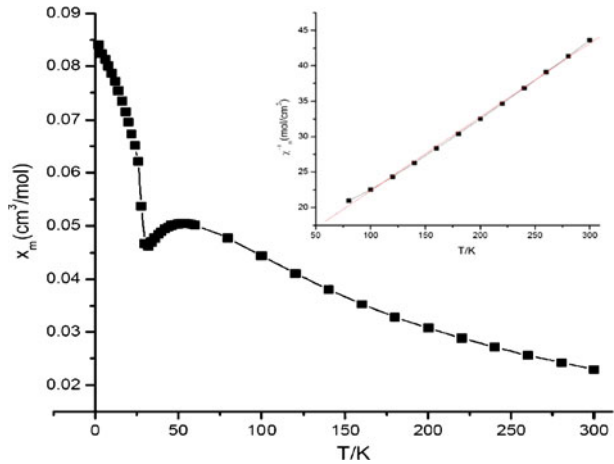
presence of hydrogen bonding. The X-ray diffraction pattern for the compound is shown in Fig. 2. The lattice parameters were determined in the refinement.

The compound  $NBu_4Fe^{II}[Fe^{III}(OX)_3]$  was characterized by powder XRD. The unit cell constants were refined on a hexagonal cell. The refined lattice parameters [7] agree well with the former results [1].

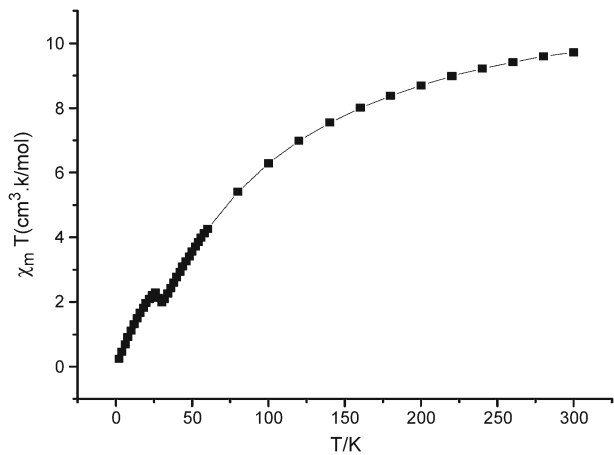
### 3.2 Magnetic analysis

The molar magnetic susceptibilities of  $NBu_4Fe^{II}_{0.07}Mn^{II}_{0.93}[Fe^{III}(OX)_3]$  at an applied field of 0.5 kOe are shown as  $\chi_m$  versus  $T$  plots in Fig. 3. The  $\chi_m$  values obey the Curie-Weiss law with a Curie constant of  $C = 9.607 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  and a Weiss paramagnetic Curie temperature of  $\theta = -114.76 \text{ K}$ . The negative  $\theta$  suggests an overall antiferromagnetic (AF) interaction in the compound, and a magnetic transition at  $-114.76 \text{ K}$ . The negative Weiss constant indicates an intramolecular

**Fig. 3**  $x_m$  vs  $T$  for  $NBu_4Fe_{0.07}^{II}Mn_{0.93}^{II}[Fe^{III}(OX)_3]$ .  
Insert: plot of  $x_m^{-1}$  versus  $T$

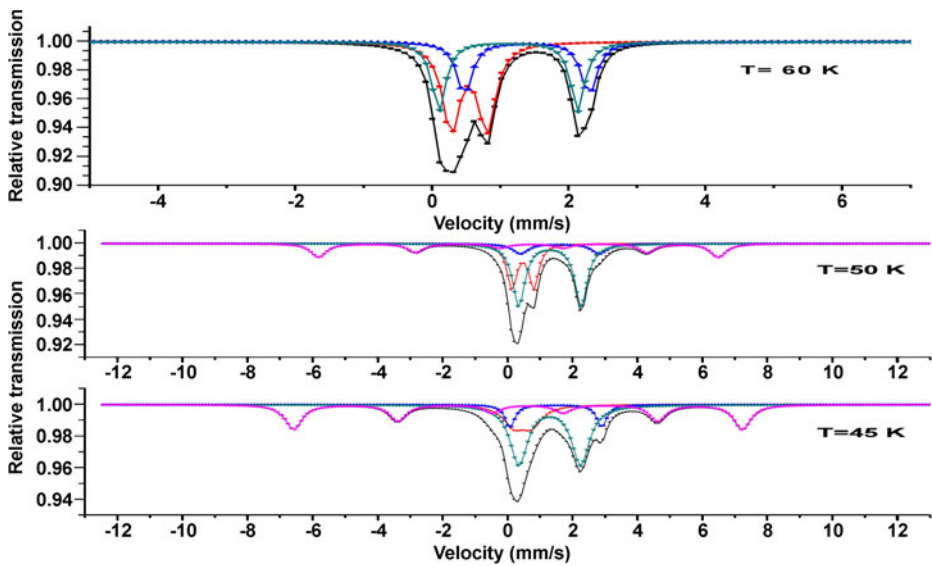


**Fig. 4**  $x_m T$  vs  $T$  for  $NBu_4Fe_{0.07}^{II}Mn_{0.93}^{II}[Fe^{III}(OX)_3]$



antiferromagnetic coupling interaction between the adjacent Fe(II) and Fe(III) ions through the oxalate bridge. The spin canted structure is compatible with the structure of the sample because of the lack of inversion center [12].

The temperature dependence of the  $x_m T$  curve for  $NBu_4Fe_{0.07}^{II}Mn_{0.93}^{II}[Fe^{III}(OX)_3]$  (as shown in Fig. 4), reveals that the material is a weak ferromagnet at low temperature. The  $x_m T$  value is  $9.03 \text{ cm}^3 \cdot \text{k} \cdot \text{mol}^{-1}$  at 300 K. Upon lowering the temperature, the  $x_m T$  values decrease gradually and reach a minimum of  $0.35 \text{ cm}^3 \cdot \text{k} \cdot \text{mol}^{-1}$  at 5 K. The abrupt increase in  $x_m T$  in the low temperature region can be attributed to a spin canting. The ferrimagnetic behavior is further characterized by measurements of the hysteresis behavior. It shows a weak coercive field  $H_C$ , typical for a soft ferromagnet. The small coercive field is consistent with the presence of magnetically isotropic ions such as Mn(II) and Fe(III) in a highly symmetrical cubic environment. The possible magnetic interaction between  $Fe^{II}(d_6, e_g^2 t_{2g}^4, S = 2)$ ,  $Fe^{III}(d_5, e_g^2 t_{2g}^3, S = 5/2)$  and  $Mn^{II}(d_5, e_g^2 t_{2g}^3, S = 5/2)$  ions may create a frustration in the magnetic interactions



**Fig. 5** Mössbauer spectrum of  $NBu_4Fe^{II}[Fe^{III}(OX)_3]$  at various temperature

between the different magnetic ion pairs, leading to a canted spin structure resulting into a weak ferromagnet or ferrimagnet.

### 3.3 Mössbauer spectroscopy

The Mössbauer spectra of  $NBu_4Fe^{II}[Fe^{III}(OX)_3]$  have been measured as a function of temperature (as shown in Fig. 5). The spectra below 50 K show three quadrupole doublets and two sextets. The two magnetically split spectra are designated as a FeIII sextet and a FeII(I) sextet. The appearance of nuclear Zeeman splitting suggests that long range magnetic ordering takes place below 50 K. In the sample, we find that the hyperfine magnetic field is proportional to the spontaneous magnetization and increases as the temperature decreases. It is worth noting that weak high-spin FeII(II) ( $S = 2$ ) resonances are present. Fishman et al. predicted inverse Jahn-Teller transitions below the ferrimagnetic transition temperature  $T_C$  in bimetallic oxalates based on first-principles calculations [13]. In the sample, the QS of both FeII(I) and FeII(II) sublattices increases markedly below 60 K. Mössbauer spectra provide strong evidence for an inverse Jahn-Teller distortion transition. It is found that the spontaneous magnetizations for FeII and FeIII sublattices have a different temperature dependence.

Mössbauer results reveal that the magnetization of the FeII sublattice increases more steeply than that of the FeIII sublattice below  $T_C$ , which gives rise to multiple magnetic-pole reversals.

We also want to address the problem of the coexistence of doublet and sextet at low temperatures. We think that the existence of a small fraction of metal vacancies, due to FeII becoming oxidized to FeIII [12–14], demolishes the near magnetic exchange interaction between FeII(I) and FeIII ions. It has also a large effect on the intraplanar cation-cation separation, the “bite”-angle subtended by the bidentate

$C_2O_4^{2-}$  bridging group and the degree of trigonal distortion around the cation sites in the compound. These effects weaken the magnetic exchange interaction between neighboring  $Fe^{II}$  (I) and  $Fe^{III}$  ions [15–17].

## 4 Conclusion

We have reported a detailed investigation of mixed-metal molecular-based magnets  $NBu_4Fe_n^{II}M_{A}^{II}{}_{1-n}[Fe^{III}(OX)_3](M_A = Mn, Fe)$ . The compound  $NBu_4Fe_{0.07}^{II}Mn_{0.93}^{II}[Fe^{III}(OX)_3]$  displays the characteristic bands of the oxalate bridging ligand. In the fitting to a Curie-Weiss law  $\chi_m = C/(T-\theta)$ , the magnetic susceptibility obeys the Curie-Weiss law with a negative Weiss constant of  $-114.76$  K. The oxalate group has been shown to be an excellent bridging ligand in supporting the magnetic exchange interaction. In the compound  $NBu_4Fe^{II}[Fe^{III}(OX)_3]$ , high-spin  $Fe^{III}$  ( $S = 5/2$ ) and  $Fe^{II}$  ( $S = 2$ ) electronic states were determined. Mössbauer results reveal that the magnetization of the  $Fe^{II}$  sublattice increases more steeply than that of the  $Fe^{III}$  sublattice below  $T_C$ , which gives rise to multiple magnetic-pole reversals. The appearance of nuclear Zeeman splitting suggests that long range magnetic ordering takes place below 50 K.

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