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Mössbauer and magnetic studies in a $Fe^{III}Mn_6^{III}$ cluster

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Abstract

Mössbauer studies confirm that the electronic state of iron is only Fe^{3+} ($S = 1/2$) in the high-nuclear cluster $[\{Mn(salen)\cdot H_2O\}_6Fe(CN)_6][Fe(CN)_6]\cdot 6H_2O$. Temperature-dependent magnetic measurements were carried out in zero-field-cooled (ZFC) and field-cooled (FC) modes. Magnetic measurements indicate the presence of intracluster ferromagnetic interaction between Fe^{III} and Mn^{III} ions.

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Keywords: Ferromagnetic interaction; Mössbauer spectroscopy; Magnetic measurements

1. Introduction

Over the past decades, the molecular-based magnets were attracting a great deal of interest. This was driven by the original magnetic properties of these systems. Recently, zero-dimension high-nuclear clusters containing the Prussian-blue analogs, which in general have high-spin ground states, were of special interest. Such complexes were prepared, including a ground $S = 15/2$ for $Cr^{III}Ni_6^{II}$ cluster, $S = 27/2$ for $Cr^{III}Mn_6^{II}$ cluster, $S = 51/2$ for $Mn_9^{II}Mo_6^{V}$ cluster, $S = 21/2$ for $Cr^{III}Mn_6^{III}$ cluster, and $S = 39/2$ for $Mn_9^{II}W_6^{V}$ cluster [1–5]. The crystal structure of first cyano-bridged-heptanuclear complex $[\{Mn(salen)\cdot H_2O\}_6Fe(CN)_6][Fe(CN)_6]\cdot 6H_2O$ had been reported by Shen et al. [6]. They also discovered that this zero-dimension cluster does not exhibit an $S = 25/2$ ground state, which is unusual enough. More Fe (III)-based high-nuclear clusters also show the abnormal behaviors [2,7]. The goal of the present study is to detect the existence of any valences and spin states of iron and magnetic behavior in $[\{Mn(salen)\cdot H_2O\}_6Fe(CN)_6][Fe(CN)_6]\cdot 6H_2O$, and to clarify its abnormal behavior.

2. Experiments

Compound $[\{Mn(salen)\cdot H_2O\}_6Fe(CN)_6][Fe(CN)_6]\cdot 6H_2O$ was obtained as microcrystal according to the procedures previously reported in Ref. [6]. The authenticity of the compound was checked by microanalyses for C, H, N, Fe, and Mn.

IR spectra were recorded on a Nicolet FT-IR NEXUS870 spectrometer with KBr pellets in the 4000–400 cm^{-1} region. The field-cooled (FC) and zero-field-cooled (ZFC) magnetization were measured by a Quantum Design MPMS-7S superconducting quantum interference device (SQUID) magnetometer.

As the radioactive source for Mössbauer measurements, ^{57}Co (Pd) moving in a constant acceleration mode was used. The sample temperature was controlled by a helium bath cryostat, and all spectra were fitted with the MössWin3.0 software. The isomer shifts are reported relative to α-Fe at room temperature.

3. Results and discussion

The Mössbauer spectra measured at various temperatures are shown in Fig. 1. These values of the isomer shift

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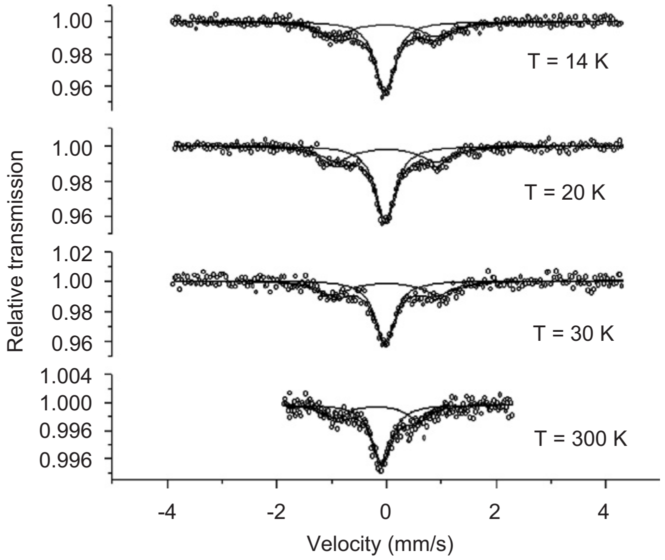

Fig. 1. Mössbauer spectra of $[\{Mn(salen)\cdot H_2O\}_6Fe(CN)_6][Fe(CN)_6]\cdot 6H_2O$ at 14, 20, 30, and 300 K.

Table 1
Mössbauer parameters of $[\{Mn(salen)\cdot H_2O\}_6Fe(CN)_6][Fe(CN)6]\cdot 6H_2O$ at various temperatures

Temp. (K)	Fe^{III}(II) singlet			Fe^{III}(I) doublet			
	IS (mm/s)	Γ (mm/s)	Area (%)	IS (mm/s)	QS (mm/s)	Γ (mm/s)	Area (%)
300	−0.08	0.42	64.7	−0.19	1.45	0.50	35.3
30	−0.025	0.45	57.6	−0.01	1.90	0.68	42.4
20	−0.019	0.45	59.9	−0.008	1.83	0.70	40.1
14	−0.020	0.43	58.5	−0.02	1.85	0.72	41.5

The isomer shift (IS) values relative to α-Fe at room temperature (with error of ± 0.02 mm/s). QS, quadrupole splitting; T, temperature.

(IS), quadrupole splitting (QS), and hyperfine magnetic field (H_{hf}) are listed in Table 1. All these Mössbauer spectra are composed of a singlet and doublet. Shen et al. [6] showed that the compound $[\{Mn(salen)\cdot H_2O\}_6Fe(CN)_6][Fe(CN)_6]\cdot 6H_2O$ contains a heptanuclear cluster $[\{Mn(salen)\cdot H_2O\}_6\times Fe(CN)_6]^{3+}$ in which the $[Fe(CN)_6]^{3-}$ unit is enclosed by six $[Mn(salen)\cdot H_2O]^+$ moieties through six bridging CN^- anions, and an isolated $[Fe(CN)_6]^{3-}$ complex balances the charge of the cluster in the compound. The local environment of the Fe(I) ion which locates in the heptanuclear cluster $[\{Mn(salen)\cdot H_2O\}_6\times Fe(CN)_6]^{3+}$ is some distortion from octahedral spherosymmetry [6]. The asymmetrical lattices and unpaired charge electron give rise to QS. A doublet is thus observed. The Fe^{III} anion in Prussian-blue analogs usually exhibits a QS ranging 0.2–1.2 mm/s in those three-dimensional compounds [8,9]. Relatively large QS values were observed for cyano-bridged complexes having low-dimension structure as a result of some distortion from cubic symmetry of $[Fe(CN)_6]^{3-}$ unit [10,11]. The negative isomer shift (IS) values indicate that the configuration of Fe^{III} ion is low-spin state, which is known to be a common spin state of Fe^{III} in various $[Fe(CN)_6]^{3-}$ complexes [8–12]. The increasing large line widths of the doublet show a dynamic behavior which means that the electric field gradient is moving from one direction to another direction in the crystal [13]. This behavior that is described in the model of Tjon and Blume is ascribable to magnetic relaxation [13]. However, the isolated $[Fe(CN)_6]^{3-}$ unit forms hydrogen bond with the hydrogen on the coordinated water molecule from the heptanuclear cation $[\{Mn(salen)\cdot H_2O\}_6\times Fe(CN)_6]^{3+}$ [6]. The singlet is assigned to the low-spin Fe^{III}(II) ($S = 1/2$) ions with octahedral symmetrical surroundings (the isolated $[Fe(CN)_6]^{3-}$) [6]. As a result of magnetic relaxation, the dynamic behavior happens also in the case of Fe^{III}(II) site. However, in this case, the quadrupole splitting contributed by unpaired charge electron is no longer observed, because the velocity of the dynamic behavior is in the fast relaxation limit [13]. In addition, these results of Mössbauer identify that Fe^{III} in the present compound is not reduced to Fe^{II}. The infrared spectra of the compound display ν_{CN} stretching bands at 2105 and 2116 cm^{-1}, indicating that the +3 oxidation state of iron is maintained, and they show both bridging and terminal CN stretches. Until the sample was cooled down to 14 K, we have not detected the magnetic splitting in the compound.

Temperature-dependent magnetic measurements were performed in FC and ZFC modes. The FC magnetization curves were obtained by cooling the sample under a field of 10 Oe. The temperature dependence of the effective magnetic moment (μ_{eff}) is shown in Fig. 2. The μ_{eff} value per Mn_6Fe_2 unit at 18 K, 12.4μ_B, is slightly higher than the value of 12.24μ_B expected for an uncoupled spin system (six $S_{Mn} = 2$, two $S_{Fe} = 1/2$). On lowering the temperature,

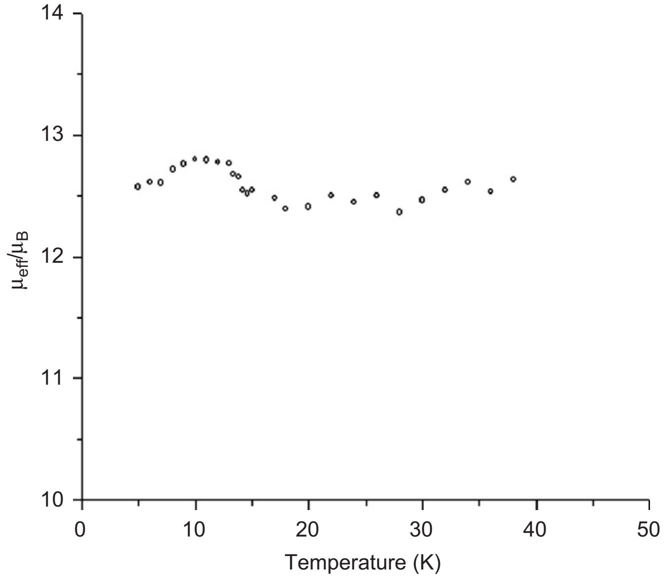

Fig. 2. Temperature dependence of the effective magnetic moment (μ_{eff}) for the present compound.