

Mössbauer Spectroscopic Studies of Molecule-Based Magnets: Two-Dimensional Complexes Derived from Metal Schiff-Bases and Hexacyanoferrate(III)

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Variable-temperature ⁵⁷Fe Mössbauer measurements on cyanide-bridged 2-D bimetallic assemblies $\text{NEt}_4[\text{Mn}(\text{salen})_2[\text{Fe}(\text{CN})_6]]$ (**1**), $\text{K}[\text{Mn}(3\text{-MeOsalen})_2[\text{Fe}(\text{CN})_6]]$ (**2**) and $\text{K}[\text{Mn}(3\text{-MeOsalen})_2[\text{Fe}(\text{CN})_6] \cdot 2 \text{DMF}$ (**3**), where $\text{salen}^{2-} = N,N'$ -ethylenebis(salicylidene iminato) dianion, revealed that these compounds exhibit a long range magnetic ordering below ca. 10 K under zero applied field. The quadrupole splittings of **1** - **3** showed intermediate values between those of typical cyano-bridged 1-D and 3-D complexes. The paramagnetic state of $\text{K}[\text{Mn}(5\text{-Clsalen})_2[\text{Fe}(\text{CN})_6] \cdot 4 \text{H}_2\text{O}$ (**4**) turned to a bulk magnetic one with desolvation.

Key words: ⁵⁷Fe Mössbauer Spectroscopy; Schiff Bases; Hexacyanoferrate(III);
Magnetic Ordering; Solvatomagnetism.

1. Introduction

In the past decade, spectacular advances have been undergone in the field of molecular magnetism [1]. An important approach to provide molecule-based materials exhibiting spontaneous magnetization is to construct ordered extended structures of paramagnetic metal centers [2]. Hexacyanometalate ions $[\text{M}(\text{CN})_6]^{x-}$ are known to be good building blocks for this purpose [2 - 15]. When $[\text{M}(\text{CN})_6]^{x-}$ reacts with simple metal ions, so-called “Prussian blue” analogues with 3-D structures of cubic lattice are formed [3 - 5]. Cationic metal-complex species, consisting of a metal ion and one or several organic ligands, also can be employed for the reaction with $[\text{M}(\text{CN})_6]^{x-}$ to construct bimetallic assemblies which are of interest from the view points of the variety of the di-

mensionality and the possible tuning of the magnetic properties by changing the ligand's chemical structure [2, 6 - 15]. Recently, Miyasaka et al. reported the syntheses and cryomagnetic properties of a series of bimetallic compounds derived from the reaction between $[\text{M}(\text{SB})]^+$ and $[\text{Fe}(\text{CN})_6]^{3-}$ of 1-D, 2-D and discrete structures (SB = quadridentate Schiff base) [6 - 11]. In order to get further information about the electronic and magnetic structure of this assembly system, we have measured ⁵⁷Fe Mössbauer spectra of three 2-D network compounds $\text{NEt}_4[\text{Mn}(\text{salen})_2[\text{Fe}(\text{CN})_6]]$ (**1**), $\text{K}[\text{Mn}(3\text{-MeOsalen})_2[\text{Fe}(\text{CN})_6]]$ (**2**) and $\text{K}[\text{Mn}(3\text{-MeOsalen})_2[\text{Fe}(\text{CN})_6] \cdot 2 \text{DMF}$ (**3**), and the related discrete trinuclear compound $\text{K}[\text{Mn}(5\text{-Clsalen})_2[\text{Fe}(\text{CN})_6] \cdot 4 \text{H}_2\text{O}$ (**4**), where $\text{salen}^{2-} = N,N'$ -ethylenebis(salicylidene iminato) dianion.

Table 1. Mössbauer parameters.

Compound	Temp./K	$\delta/\text{mm}\cdot\text{s}^{-1}$	$\Delta E_Q^a/\text{mm}\cdot\text{s}^{-1}$	H_n/kOe
1 ^b	298	-0.13	1.06	
	78	-0.05	1.30	
	4.2	-0.03	1.43	127
2	298	-0.09	1.40	
	78	-0.07	1.70	
	4.2	-0.05	1.87	119
3	298	-0.10	0.68	
	78	-0.08	1.12	
	4.2	-0.06	1.26	115
4	298	-0.13	1.45	
	4.2	-0.05	1.81	
	Desolvated 4	298	-0.15	1.43
	4.2	~ 0.0	~ 1.5	~ 230

^a The sign of V_{zz} was not determined. ^b For example, the analysis of the spectrum of **1** at 4.2 K gives the other following parameters: $\eta = 0.5 - 1.0$, $|\frac{1}{2}eV_{zz}Q| = 1.37 - 1.23 \text{ mm/s}$, $\Theta = 52^\circ$, $\varphi = 10^\circ$, on the assumption of $V_{zz} > 0$; $\eta = 0.1 - 1.0$, $|\frac{1}{2}eV_{zz}Q| = 1.43 - 1.23 \text{ mm/s}$, $\Theta = 71 - 82^\circ$, $\varphi = 25 - 40^\circ$, on the assumption of $V_{zz} < 0$. Here, the symbols have the usual meanings [19].

2. Experimental

The compounds **1** - **4** were prepared according to procedures previously reported [7, 11]. The Mössbauer spectra were measured between 4.2 and 298 K by using a $^{57}\text{Co}(\text{Rh})$ source moving in a constant acceleration mode. The isomer shifts are reported relative to metallic iron foil. The samples were sealed in containers consisting of a Cu block and Mylar films for the measurements.

3. Results and Discussion

Compounds **1** and **2** were reported to have similar crystal structures [7, 11]. In each compound, two CN^- groups of the $[\text{Fe}(\text{CN})_6]^{3-}$ moiety bridge two Mn ions to give a linear bridging mode of (SB)Mn-NC-Fe-CN-Mn(SB). Two other CN^- groups of the $[\text{Fe}(\text{CN})_6]^{3-}$ moiety are bound to the adjacent chains, producing a two-dimensional network structure in which a net unit has a cyclic octamer structure [-Mn-NC-Fe-CN]₄. The counter anions (NEt_4^+ or K^+) are sandwiched between the network layers. Cryomagnetic measurements indicated that an intralayer antiferromagnetic interaction operates between the Mn(III) and the Fe(III) ions in **1**, and that the compound orders ferrimagnetically below the critical temperature, $T_c = 7.7 \text{ K}$ [11]. As for **2**, intralayer ferromagnetic and interlayer anti-ferromagnetic interactions were observed, and **2** be-

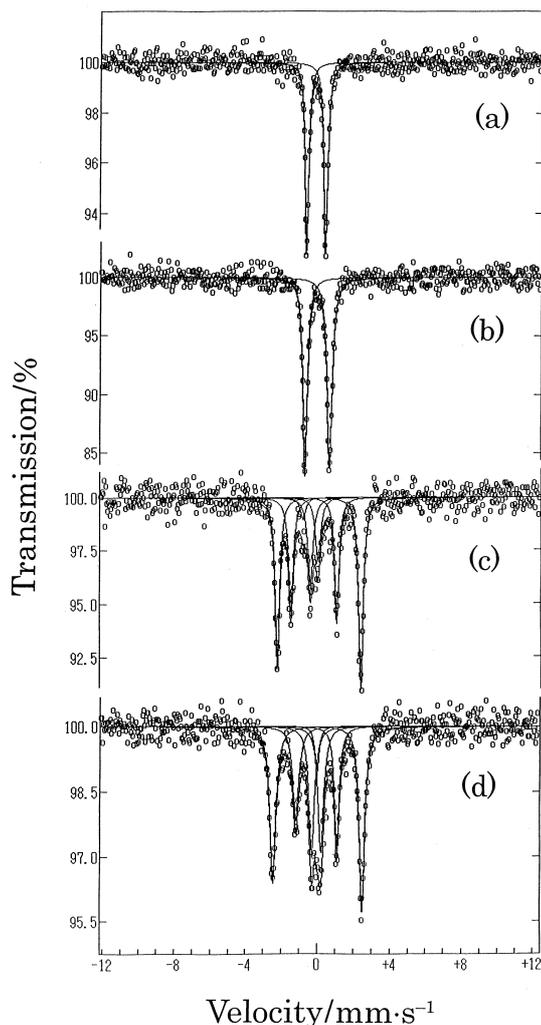


Fig. 1. ^{57}Fe Mössbauer spectra of $\text{NEt}_4[\text{Mn}(\text{salen})_2][\text{Fe}(\text{CN})_6]$ (**1**) at (a) 298 K, (b) 10 K, and (c) 4.2 K, and (d) ^{57}Fe Mössbauer spectrum of $\text{K}[\text{Mn}(3\text{-MeOsalen})_2][\text{Fe}(\text{CN})_6]$ (**2**) at 4.2 K.

has as a metamagnet with variable T_c (ca. 8 - 10 K) depending on the applied field [7].

Selected Mössbauer spectra of **1** and **2** are shown in Fig. 1, and their Mössbauer parameters are listed in Table 1 along with those of the other compounds mentioned below. Compound **1** gave a single quadrupole doublet above 10 K, showing an ordinary paramagnetism of Fe(III) (Figs. 1a, b). The low isomer shift, δ ($\sim 0.0 \text{ mm/s}$), and the temperature-dependent quadrupole splitting, ΔE_Q , observed were characteristic of a low-spin Fe(III) state [16], which is known to be a common spin state of Fe(III) in vari-

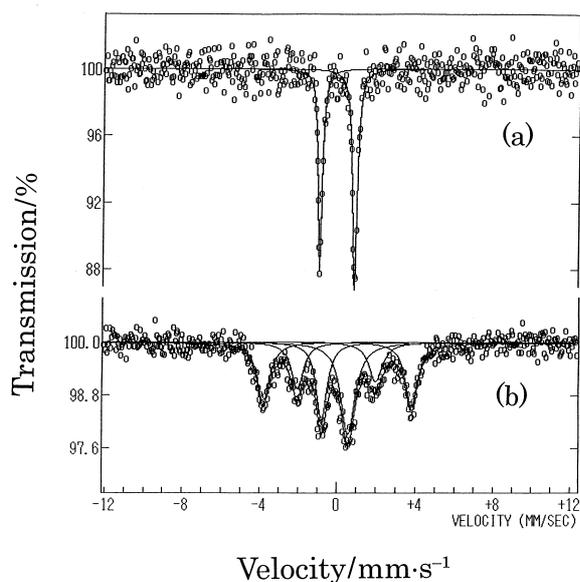


Fig. 2. ^{57}Fe Mössbauer spectra at 4.2 K of (a) $\text{K}[\text{Mn}(\text{5-Cl salen})_2][\text{Fe}(\text{CN})_6] \cdot 4 \text{H}_2\text{O}$ (**4**) and (b) desolvated **4**.

ous $[\text{Fe}(\text{CN})_6]^{3-}$ complexes [2 - 15]. On lowering the temperature to 8 K, a line-broadening began to appear in the spectrum of **1**, and at 4.2 K, a sharp Mössbauer septet was observed as shown in Fig. 1c. This sudden change of the line-shape of a Mössbauer spectrum in a narrow temperature range evidences long range magnetic ordering below ca. 8 K, under zero applied field. The temperature-dependence of the spectrum shape of **2** was very similar to that of **1**, also giving a well-resolved septet at 4.2 K (Fig. 1d). While the previous cryomagnetic results for **2** showed some complexity (due to metamagnetism) [7], this Mössbauer behavior clearly indicated the bulk magnetic ordering of **2** at low temperatures.

The ΔE_Q values of compounds **1** and **2** (for example, 1.30 and 1.70 mm/s at 78 K, respectively) were larger than those of the $[\text{Fe}(\text{CN})_6]^{3-}$ anions in Prussian blue analogues ranging ca. between 0.2 and 1.0 mm/s around and below liquid nitrogen temperature (77.3 K) [17]. This would reflect the low-dimensionality (2-D structure) of these compounds, resulting in a considerable deviation of the $[\text{Fe}(\text{CN})_6]^{3-}$ unit from cubic symmetry, as seen in the X-ray crystallographic data of **1** [11]. (The exact crystal structure of **2** is not known [7].) As for the 1-D

ciano-bridged complexes, ΔE_Q values > 2.0 mm/s were sometimes obtained; for examples, 2.44 mm/s at 78 K for $[\text{Mn}(\text{cyclam})][\text{Fe}(\text{CN})_6] \cdot 3 \text{H}_2\text{O}$ [15] and 2.56 mm/s at 78 K for $\{[\text{Eu}(\text{phen})_2(\text{H}_2\text{O})_2][\text{Fe}(\text{CN})_6] \cdot 2\text{phen}\}_x$ [18], where cyclam = 1,4,8,11-tetraazacyclotetradecane and phen = 1,10-phenanthroline. The magnitudes of the internal magnetic field (H_n) were estimated [19] to be 127 and 119 kOe for **1** and **2**, respectively. They are very close to the spin-polarized Hartree-Fock estimation (125 kOe) [20]. On the other hand, much larger H_n values were reported for the $[\text{Fe}(\text{CN})_6]^{3-}$ in Prussian blue analogues (160 - 270 kOe), and the deviation from the calculated value was ascribed to a large delocalization of 3d electrons *via* back donation [3], which would be insignificant in the present compounds containing metal-complex cations. The smaller ΔE_Q value (1.12 mm/s at 78 K) of **3** than that of **2** suggests that the inclusion of DMF molecules in the crystal lattice of **2** decreases the extent of distortion of the $[\text{Fe}(\text{CN})_6]^{3-}$ anion. No substantial difference in the magnetic-splitting behavior was observed between **2** and **3**.

Compound **4** was reported to be a discrete trinuclear compound with linear Mn-NC-Fe-CN-Mn linkage, and to act as a paramagnet at least above 4.2 K [7]. The Mössbauer spectrum of **4** consisted of a quadrupole doublet even at 4.2 K (Fig. 2a), in accord with the cryomagnetic result. After the compound was heated at 40 °C under a pressure of 10^{-4} Pa for 24 h, it gave a quite different spectrum at the same temperature, as seen in Fig. 2b, which indicates the occurrence of bulk magnetic ordering. Elemental analyses roughly showed the loss of two water molecules from **4** by the heat treatment. Similarly to the case of the NEt_4 analogue of **4** [8], an extended structure formation by desolvation seems to occur in the crystal lattice of **4**. However, the broadened spectral feature suggested that the structure of desolvated **4** is not uniform, and the H_n value was significantly different from those of **1** - **3**. By the re-wetting of desolvated **4**, its spectrum at 4.2 K reverted to a quadrupole doublet. Another kind of "solvatomagnetism", where desolvation causes a transition from a bulk magnetic state to a paramagnetic one, is currently being investigated for $[\text{Fe}(\text{salen})(\text{CH}_3\text{OH})_2][\text{Fe}(\text{salen})_2][\text{Fe}(\text{CN})_6] \cdot 3 \text{H}_2\text{O}$ [11] by ^{57}Fe Mössbauer spectroscopy.

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