



Cyanide-Bridged Heterobimetallic Fe(III)-Mn(II) Complex: Synthesis, Crystal Structure and Magnetic Property

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A cyanide-bridged heterobimetallic trinuclear Fe(III)-Mn(II) complex with the formula $\{[\text{Fe}(\text{pcq})(\text{CN})_3]_2[\text{Mn}(\text{CH}_3\text{OH})_4]\}$ (**1**) has been synthesized with *mer*- $[\text{PPh}_4][\text{Fe}(\text{pcq})(\text{CN})_3]$ (*pcq* = 8-(pyridine-2-carboxamido)quinoline anion) as building block and $[\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}]$ as assemble segment. Single X-ray diffraction reveals its neutral trinuclear Fe_2Mn nature, in which the two cyanide-containing building blocks acting as a monodentate ligand are coordinated to the central Mn(II) ion. Investigation over its magnetic property shows the antiferromagnetic magnetic coupling between the cyanide-bridged neighboring Fe(III) and Mn(II) ions.

Keywords: Cyanide-bridged, Crystal structure, Magnetic property.

INTRODUCTION

As a remarkable magnetic linker that can mediate efficient ferro- or antiferromagnetic exchange interactions between paramagnetic centers depending on the structural parameters, polycyanidometallates are the most extensively used metallo-ligands with which to prepare molecule-based magnetic materials with diverse architectures and interesting magnetic properties¹⁻³. The rational design of cyanide-bridged materials can be achieved following a building-block approach with the premeditated association of various complexes and capped polycyanidometallates $[\text{M}(\text{L})_x(\text{CN})_y]^{z-}$ (*L* = mono- or multi-dentate ligand) that promote compounds with low dimensionality⁴⁻⁶.

The cyanide precursor *mer*- $[\text{Fe}^{\text{III}}(\text{pcq})(\text{CN})_3]^-$ is firstly developed by our group to prepare low-dimensional cyanide-bridged system⁷. After that, several *mer*- $[\text{Fe}^{\text{III}}(\text{L}')(\text{CN})_3]^{2-}$ (*L'* = tridentate ligand) building blocks have also been designed and employed to synthesize polynuclear or one-dimensional cyanide-bridged complexes⁸⁻¹². In this paper, a trinuclear cyanide-bridged Fe(III)-Mn(II) complex based-on *mer*- $[\text{Fe}^{\text{III}}(\text{pcq})(\text{CN})_3]^-$ ion with the formula $\{[\text{Fe}(\text{pcq})(\text{CN})_3]_2[\text{Mn}(\text{CH}_3\text{OH})_4]\}$ (**1**), including its synthesis, crystal structure and magnetic property, will be described.

EXPERIMENTAL

A colorless CH_3OH solution (10 mL, *v/v* = 2:1) of $[\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}]$ (0.1 mmol, 36.5 mg) was carefully layered onto a dark red DMF solution (10 mL) of *mer*-

$[\text{PPh}_4][\text{Fe}(\text{pcq})(\text{CN})_3]$ (0.2 mmol, 142.2 mg). After the mixture was stood for a few days in the dark box with the aim to avoid decomposing the cyanide-containing building block, dark brown crystals suitable for X-ray diffraction were obtained. They were collected by filtration, washed with cooled methanol and dried at room temperature. Yield: 54.7 mg, 57.7 %. Anal. Calcd. for $\text{C}_{40}\text{H}_{36}\text{N}_{12}\text{O}_6\text{Fe}_2\text{Mn}$: C, 50.71; H, 3.83; N, 14.74. Found: C, 50.74; H, 3.78; N, 14.61.

Physical measurements: Elemental analyses of carbon, hydrogen and nitrogen were carried out with an Elementary Vario El. Variable-temperature magnetic susceptibility and field dependence magnetization measurements were performed on a Quantum Design MPMS SQUID magnetometer.

Structure determination: Data were collected on an Oxford Diffraction Gemini E diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. Final unit cell parameters were derived by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated by using the preliminary cell-orientation matrix. CrysAlisPro Agilent Technologies software was used for collecting frames of data, indexing reflections and determination of lattice constants; CrysAlisPro Agilent Technologies for integration of intensity of reflections and scaling, SCALE3 ABSPACK for absorption correction. The structures were solved by the direct method (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97) on F^2 ¹³. Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. Crystallographic

data and experimental details for structural analyses are summarized in Table-1. CCDC: 958123.

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE
REFINEMENT SUMMARY FOR THE COMPLEX

Empirical formula	C ₄₀ H ₃₆ N ₁₂ O ₆ Fe ₂ Mn
Formula weight	947.75
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions (Å)	A = 20.389(3), b = 14.2894(10), c = 15.606(2)
Volume (Å ³)	4155.2(8)
Z, Calculated density (mg/m ³)	4, 1.515
Absorption coefficient	1.051
F(000)	1940
Reflections collected/unique	8059/3656
Data/restraints/parameters	3656/2/278
Goodness-of-fit on F ²	1.009
Final R indices [I > 2 σ (I)]	0.0658
R indices (all data)	0.1185
Largest diff. peak and hole (e/Å ³)	0.628 and -0.629

RESULTS AND DISCUSSION

Some important structural parameters for complex **1** are collected in Table-2. The molecular structure for the complex **1** and its supramolecular structure are shown in Figs. 1 and 2, respectively. As can be found, complex **1** crystallizes in monoclinic space group C2/c, containing four independent units in the unit cell. Complex **1** is composed of neutral trinuclear entity with the formula $\{[\text{Fe}(\text{pcq})(\text{CN})_3]_2[\text{Mn}(\text{CH}_3\text{OH})_4]\}$, in which the two $[\text{Fe}(\text{pcq})(\text{CN})_3]$ units, acting as a mono-dentate ligand, connect the central Mn(II) ion coordinated by the additional four O atoms coming from four methanol molecules. The coordination sphere for both of the Fe(III) atom and the Mn(II) atom is slightly distorted octahedron. The Fe(III) atom is surrounded by a C₃N₃ unit, while the six coordination positions of the Mn(II) atom are occupied by two N atoms of the bridged cyanide groups and four O atoms coming from the four coordinated methanol molecules. As shown in Table-2, the distances between the Mn atom and the O atoms of the solvent molecules are 2.204(4) and 2.175(4) Å, while the Mn-N cyanide bond lengths are 2.172(5) Å, giving further information about the slightly distorted geometry of the Mn(II) ion. The intramolecular Fe-Mn separation through bridging cyanide is 5.279 Å, which is obviously the shorter than the intermolecular metal-metal separation 7.739 Å. It is worth noting that complex **1** can be linked into three-dimensional supramolecular network under the help of the intermolecular O-H...N hydrogen bond interactions.

TABLE-2
SELECTED BOND LENGTHS (Å) AND
ANGLES (°) FOR THE COMPLEX

Bond	Dist.	Bond	Dist.	Bond	Dist.
Mn1-N1	2.172(5)	Mn1-O1	2.204(4)	Mn1-O2	2.175(4)
Fe1-C1	1.939(6)	Fe1-C2	1.932(7)	Fe1-C3	1.945(7)
Fe1-N4	1.950(4)	Fe1-N5	1.888(4)	Fe1-N6	1.960(4)
Angle	(°)	Angle	(°)	Angle	(°)
Mn1-C1-N1	175.7(5)	C2-Fe1-C3	170.2(2)	Fe1-C1-N1	179.8(7)

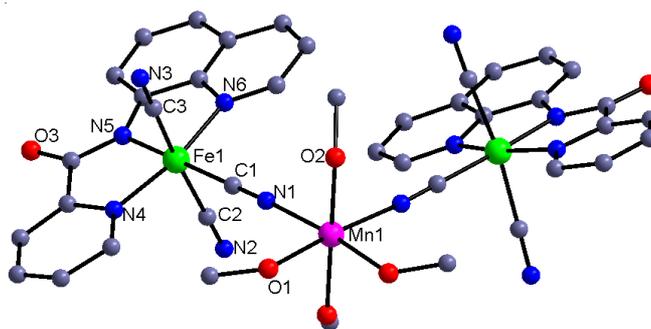


Fig. 1. Molecular structure of complex **1**

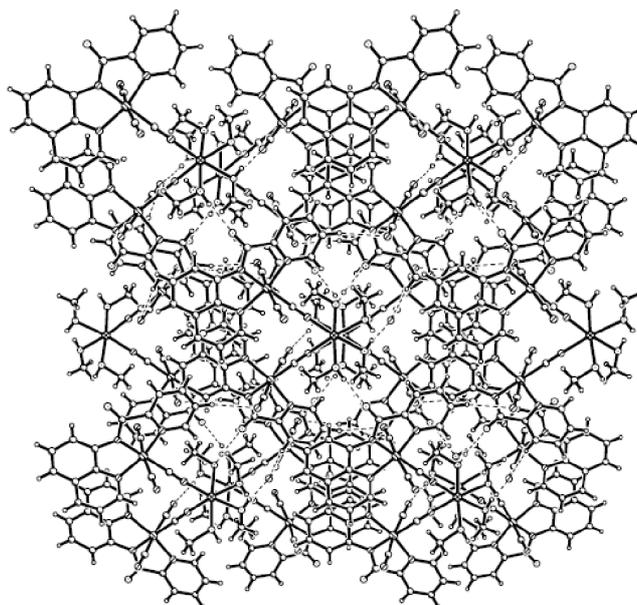


Fig. 2. 3D supramolecular structure of complex **1** formed by the intermolecular H-bond interactions

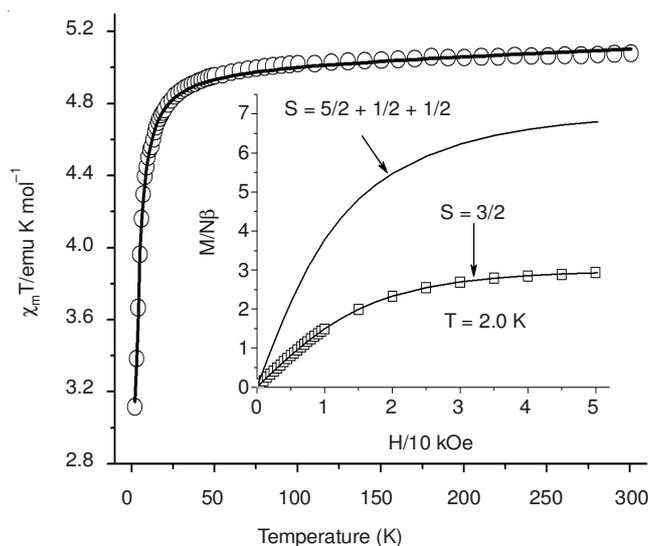


Fig. 3. Magnetic properties of complex **1**

The temperature dependence of magnetic susceptibility for the complex measured in the temperature range of 2-300 K in the applied field of 2000 Oe is given in Fig. 3. The room temperature $\chi_m T$ values of the complex is 5.08 emu K mol⁻¹, which is consistent with the spin only value of 5.125 emu K

mol⁻¹ for uncoupled Mn(II) ($S = 5/2$) and two low spin Fe(III) ($S = 1/2$) based on $g = 2$. With the temperature decreasing, the $\chi_m T$ value decreases gradually and attains the value of 4.90 emu K mol⁻¹ at about 50 K, then decreases sharply to their lowest value of 3.11 emu K mol⁻¹ at 2 K. This is characteristic of antiferromagnetic coupling in the trimeric Fe^{III}₂Mn^{II} cluster, which is also proven by the Brillouin curves (Fig. 3). The magnetic susceptibility for the complex conforms well to Curie-Weiss law in the range of 2-300 K and give the negative Weiss constant $q = -3.17$ K and Curie constant $C = 5.10$ emu K mol⁻¹.

On the basis of the trimeric model, the magnetic susceptibilities of complex **1** can be fitted accordingly by the following expression derived from the isotropic exchange spin Hamilton $H = -2J\hat{S}_{Mn}(\hat{S}_{Fe(1)} + \hat{S}_{Fe(2)})$ in which the magnetic interactions between the terminal Fe(III) ions have been neglected.

$$\chi_m = \frac{Ng^2\beta^2}{4kT} \left[\frac{10\exp(-7J/kT) + 35\exp(-2J/kT) + 35 + 84\exp(5J/kT)}{2\exp(-J/kT) + 3\exp(-2J/kT) + 3 + 4\exp(5J/kT)} \right]$$

$$\chi_t = \frac{\chi_m}{1 - \chi_m(2zJ'/Ng^2\beta^2)}$$

The best-fit parameters obtained are $J = -1.02(2)$ cm⁻¹, $g = 1.99(2)$, $zJ' = -0.13(7)$ cm⁻¹, $R = \Sigma(\chi_{\text{obsd}}T - \chi_{\text{calcd}}T)^2 / \Sigma(\chi_{\text{obsd}}T)^2 = 1.26 \times 10^{-5}$. These values are comparable with those of Fe^{III}2Mn^{II} complexes reported recently^{7,14,15}.

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