Cyanide-Bridged Polynuclear and One-Dimensional Fe^{III}-Mn^{III/II} Bimetallic Complexes Based-on Pentacyanoferrite(III) Building Block: Synthesis, Crystal Structures, and Magnetic Properties

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Abstract

In this contribution, based-on the structurally confirmed pentacyanometallate (PPh₄)₂[Fe(CN)₅(imidazole)]·(imidazole)·H₂O (1) and the manganese compounds [Mn(L)(H₂O)₂]ClO₄ (L = N,N-ethylenebis(3-methoxysalicylideneimine) or [Mn(MAC)(H₂O)Cl]ClO₄ (MAC = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo-[12.3.1]octadeca-1(18),2,12,14,16-pentaene), two new cyanide-bridged bimetallic Fe^{III}-Mn^{III/II} complexes {[Mn(L)(H₂O)]₃[Fe(CN)₅(imidazole)]}(ClO₄) (2) and {[Mn(MAC)]₂[Fe(CN)₅(imidazole)]·CH₃OH}_n (3) were successfully synthesized and characterized by elemental analysis, IR spectroscopy and X-ray structure determination. Single X-ray diffraction analysis reveals the cationic FeMn₃ tetranuclear entity for complex 2, which can be further assembled into supramolecular 1D ladder-like double chain by the strong intermolecular hydrogen bond interactions. For complex 3, it can be structurally characterized as neutral one-dimensional linear single infinite chain. The magnetic investigations discover the ferromagnetic coupling between the Fe^{III}-Mn^{III} units in complex 2 and the antiferromagnetic coupling in complex 3 between the Fe^{III}-Mn^{II} units through the bridging cyanide group, respectively.

Keywords: Pentacyanoferrite; cyanide-bridged; crystal structure; magnetic property

1. Introduction

In the past several decades, due to their great potential in high-tech fields including quantum compute, information storage, etc., more and more attention have been paid to the research of the molecular-based magnetism.^{1–8} As one of the most important building block for the rational construction of molecular magnetic systems, cyanide-bridged magnetic complexes have all along received intense attention since their readily controlled molecular topological structures and theoretically predicted magnetic properties.^{9–13} Up to now, a great deal of cyanide-bridged molecular materials structural ranging from 0-dimensional cluster to three-dimensional beautiful networks have been rationally designed and structurally characterized.

Among those, some systems with interesting magnetic properties, such as single chain magnets (SCMs) and single molecule magnets (SMMs),^{14–20} spin crossover materials,^{21–23} high-T_c magnets,^{24–25} photomagnetic materials,^{26–29} ferromagnetic materials,³⁰ chirality magnets^{31–33} et al, have been detailed magnetically studied.

One of the most successful strategies used to prepare cyanide-bridged magnetic complexes^{34–35} is based on the assemble reactions of the decorated polycyanometallates [M(L)(CN)_x]ⁿ⁻ ((M = Fe, Cr, W, Mo, Mn, Ru; x = 1–8, L = mono- or multi-dentate organic ligand) with other counterpart paramagnetic metal compounds. Because the blocking organic ligand(s) in either the cyano precursors or the counterpart assemble segments can contribute obvious steric effect and therefore efficiently lower the dimen-

Scheme 1. The starting materials used in this paper.

sionality of the target product, many low-dimensional $[M(L)(CN)_x]^{n-}$ -based complexes have been expectedly obtained.^{36–38} Among all the polycyanoferrite(III) building blocks, the pentacyanoferrite(III) $[Fe(L)(CN)_5]^{2-}$ (L = monodentate ligand) precursors have been comparatively limited employed in cyanide-bridged molecule magnetism field.^{39–43} In this paper, we are focusing on the designed preparation of new cyanide-bridged magnetic complexes with the exploitation of pentacyanideferrite(III) compound $[Fe(CN)_5(imidazole)]^{2-}$ as building block and manganese compounds as assemble segments (Scheme 1). The synthesis, structural characterization and magnetic study for the two new obtained $Mn^{II/III}$ - Fe^{III} bimetallic magnetic complexes $\{[Mn(L)(H_2O)]_3[Fe(CN)_5(imidazole)]\}(ClO_4)_4$ (**2**) and $\{[Mn(MAC)]_3[Fe(CN)_5(imidazole)]\}(CH_3OH)_n$ (**3**), as well as the structure of the cyano precursor $(PPh_4)_2[Fe(CN)_5(imidazole)] \cdot (imidazole) \cdot H_2O$ (**1**), will be presented in the current contribution.

2. Experimental Section

2.1. General Procedures and Materials

All the reactions were carried out at room temperature under air atmosphere with the solvents and chemicals used reagent grade without additional purification. $[Ca(imidazole)(H_2O)][Fe(CN)_5(imidazole)]$ was prepared as black crystals according to the literature method for $[Ca(1-CH_3im)(H_2O)][Fe(CN)_5(1-CH_3im)]$.⁴¹ $[Mn(L)(H_2O)_2]ClO_4$ ⁴² (L = N,N-ethylenebis(3-methoxysalicylideneimine) and $[Mn(MAC)(H_2O)Cl]ClO_4$ ⁴⁴ (MAC = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo-[12. 3.1]octadeca-1(18),2,12,14,16-pentaene) were available from the previous works.

Caution! KCN is hypertoxic and hazardous. Perchlorate salts with organic ligands are potentially explosive. They should be handled in small quantities with care.

Synthesis of $(PPh_4)_2[Fe(CN)_5(imidazole)] \cdot (imidazole) \cdot H_2O$ (**1**):

$[Ca(imidazole)(H_2O)][Fe(CN)_5(imidazole)]$ (1.9 g, 5 mmol) was dissolved in water (20 ml), and PPh_4Br (4.0 g,

10 mmol) was added to the solution. Then, the mixture was stirred in the dark overnight before the yellow powder formed was filtered out. Yield: 3.57g (70%). Recrystallization of the powder in MeOH afforded yellow single crystals. Main IR bands(cm^{-1}): 2110, 2121(s, $\nu_{C\equiv N}$). The elemental analysis (experimental and theoretical) and some physical properties are given in Table 1.

Synthesis of $\{[Mn(L)(H_2O)]_3[Fe(CN)_5(imidazole)]\}(ClO_4)_4$ (**2**):

The complex was prepared by using three layers diffusion procedure. A solution containing $(PPh_4)_2[Fe(CN)_5(imidazole)] \cdot (imidazole) \cdot H_2O$ (102 mg, 0.10 mmol) dissolved in 5 mL H_2O was laid in the bottom of a tube, and then carefully upon addition of a mixture solvent of water and methanol (5 mL) with a ratio of 1:1. Finally, a solution of $[Mn(L)(H_2O)_2]ClO_4$ (112 mg, 0.2 mmol) in 5 mL of CH_3OH was carefully added to the top of the mixture solvent layer above formed. The dark-brown crystal appeared in the middle of the tube was filtered out 2–3 weeks later, washed by methanol and dried in air. $\{[Mn(L)(H_2O)]_3[Fe(CN)_5(imidazole)]\}(ClO_4)_4$ (**2**): Yield: 49.6 mg (44.6%). Main IR bands(cm^{-1}): 2150 (s, $\nu_{C\equiv N}$), 2122 (s, $\nu_{C\equiv N}$), 1620 (m, $\nu_{C\equiv N}$), 1100 (s, $\nu_{Cl=O}$). The elemental analysis (experimental and theoretical) and some physical properties are given in Table 1.

Synthesis of $\{[Mn(MAC)][Fe(CN)_5(imidazole)]\} \cdot CH_3OH\}_n$ (**3**):

A solution of $(PPh_4)_2[Fe(CN)_5(imidazole)] \cdot (imidazole) \cdot H_2O$ (102 mg, 0.10 mmol) dissolved in 5 mL H_2O was laid in the bottom of a tube, and then carefully upon addition of a mixture solvent of water and methanol (5 mL) with a ratio of 1:1. Finally, a solution of $[Mn(MAC)(H_2O)Cl]ClO_4$ (48 mg, 0.1 mmol) in 5 mL of CH_3OH was carefully added to the top of the mixture solvent layer above formed. The yellow crystal appeared in the middle of the tube 2–3 weeks later, which was filtered out, washed by methanol and dried in air. $\{[Mn(MAC)][Fe(CN)_5(imidazole)]\} \cdot CH_3OH\}_n$ (**3**): Yield: 43.6 mg, 70.9%. Main IR bands (cm^{-1}): 2150, 2120(s, $\nu_{C\equiv N}$), 1630 (m, $\nu_{C\equiv N}$). The elemental analysis (experimental and theoretical) and some physical properties are given in Table 1.

Table 1. The elemental analysis (experimental and theoretical) and some physical properties for complexes 1–3.

Formula	Elemental Analysis(Cal.)	Elemental Analysis(Found)	Color	Solubility	Melting Point
C ₅₉ H ₅₀ N ₉ O P ₂ Fe	C, 69.55; H, 4.95; N, 12.37	C, 69.62; H, 5.01; N, 12.31	Yellow	MeOH	> 573K
C ₆₉ H ₈₀ N ₁₃ O ₂₀ ClFeMn ₃	C, 49.70; H, 4.84; N, 10.92.	C, 49.77; H, 4.91; N, 11.00	Dark- Brown	MeOH DMF	> 573K
C ₂₄ H ₃₁ N ₁₂ OFeMn	C, 46.92; H, 5.09; N, 27.36	C, 46.86; H, 5.16; N, 27.47	Yellow	MeOH DMF	> 573K

2. 2. X-ray Data Collection and Structure Refinement

Single crystals with suitable dimensions for complexes 1–3 for X-ray diffraction analysis were mounted on the glass rod and the crystal data were collected on a Bruker APEX II CCD area-detector with a Mo K α sealed tube ($\lambda = 0.71073 \text{ \AA}$) at room temperature using a ω scan mode. The structures were solved by direct method and expanded using Fourier difference techniques with the SHELX-TL-2018/3 program package.⁴⁵ While all the hydrogen atoms were introduced as fixed contributors, the non-hydrogen atoms were refined anisotropically with anisotropic displacement coefficients. Hydrogen atoms except some ones from the solvent molecules were assigned isotropic displacement coefficients $U(H) = 1.2U(C)$ or $1.5U(C)$ and their coordinates were allowed to ride on their respective carbon/nitrogen atoms using SHELXL 2018/3. For the solvent H atoms, they were refined isotropically with fixed U values, during which the DFIX command was used to rationalize the bond parameter. The CCDC 1978692–1978694 for complexes 1–3 contain the

supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Details of the crystallographic parameter, data collection, and refinement are summarized in Table 2.

3. Results and Discussion

3. 1. Synthesis

With comparison to the widely used hexacyanoiron(III) in cyanide-bridged molecular magnetism field, the pentacyanoiron(III) has been relatively less used to assemble magnetic complex, and only several pentacyanoiron(III)-based heterometallic magnetic systems have been reported.^{39–42, 45} By using the three-layers diffusion method, which has been shown to be a powerful way for growing single crystals,^{43–44} one cationic tetranuclear Fe^{III}Mn^{III}₃ entity and one neutral one-dimensional Fe^{III}Mn^{II} complex have been successfully prepared from the reactions of [Fe(imidazole)(CN)₅]^{2–} and the manganese

Table 2. Details of the crystal parameters, data collection, and refinement for compounds 1–3.

	1	2	3
Formula	C ₅₉ H ₅₀ N ₉ O ₂ P ₂ Fe	C ₆₉ H ₈₀ N ₁₃ O ₂₀ ClFeMn ₃	C ₂₄ H ₃₁ N ₁₂ OFeMn
Fw	1018.87	1667.58	614.4
Crystal system	monoclinic	monoclinic	Triclinic
Space group	P21/c	C 2/c	P-1
a/ $\text{\AA}$	12.8623(7)	45.062(5)	10.883(3)
b/ $\text{\AA}$	23.5860(13)	13.5410(14)	11.521(3)
c/ $\text{\AA}$	18.4068(9)	29.308(4)	13.284(3)
α/deg	90	90	90.578(4)
β/deg	106.7580(10)	116.647(4)	105.693(4)
γ/deg	90	90	114.939(4)
Z	4	8	2
V/ $\text{\AA}^3$	5346.9(5)	15984(3)	1439.1(6)
F(000)	2124	6904	636
θ/deg	1.65–25.01	1.59–25.01	1.61–25.01
Goodness-of-fit	1.016	1.019	1.046
R ₁ [$I > 2\sigma(I)$]	0.0459	0.0659	0.0692
wR ₂ (all data)	0.1166	0.2125	0.2086

Scheme 2. The preparation diagram for the complex **2** and **3**.

Schiff-base $[\text{Mn}(\text{L})]^+$ or the macrocyclic $[\text{Mn}(\text{MAC})]^{2+}$ compound, respectively (Scheme 2).

The cyanide-bridged heterometallic complexes have been characterized by IR spectroscopy. Compared to the cyanide precursor with only one peak at about 2125 cm^{-1} , two sharp peaks in the IR spectra of complexes **2** and **3** due to the cyanide-stretching vibration [42, 43] were observed at about 2120 and 2160 cm^{-1} , respectively, indicating the presence of bridging and nonbridging cyanide ligands in these complexes. For complex **2**, the strong peak centered at 1100 cm^{-1} is attributed to the free ClO_4^- anions.

3. 2. Crystal Structure Descriptions

The crystal structure of the cyano precursor:

The selected bond lengths and angles for complex **1** are given in Table 3. The molecular structure and the H-bond resulted 1D supramolecular structure are shown in

Figures 1 and 2, respectively. The asymmetric unit of $(\text{PPh}_4)_2[\text{Fe}(\text{CN})_5(\text{imidazole})] \cdot (\text{imidazole}) \cdot \text{H}_2\text{O}$ (**1**), which crystallizes in monoclinic space group $\text{P}2_1/\text{c}$, is comprised

Table 3. Selected bond lengths (Å) and angles (°) for complex **1**.

Complex 1			
Fe(1)-N(1)	2.002(2)	P(1)-C(12)	1.793(3)
Fe(1)-C(4)	1.951(3)	P(1)-C(18)	1.786(3)
Fe(1)-C(5)	1.949(3)	P(1)-C(24)	1.789(3)
Fe(1)-C(6)	1.925(3)	P(1)-C(30)	1.797(3)
Fe(1)-C(7)	1.951(3)	P(2)-C(36)	1.789(3)
Fe(1)-C(8)	1.958(3)	P(2)-C(42)	1.797(3)
Fe(1)-C(4)-N(3)	179.2(3)	P(2)-C(48)	1.793(3)
Fe(1)-C(5)-N(4)	175.4(3)	P(2)-C(54)	1.787(3)
Fe(1)-C(6)-N(5)	176.3(3)	Fe(1)-C(8)-N(7)	178.4(2)
Fe(1)-C(7)-N(6)	177.9(3)

Figure 1. The molecular structure of complex **1**. The solvent molecule, the co-crystallized imidazole and all the H atoms have been omitted for clarity.

Figure 2. The H-bond resulted 1D anionic supramolecular structure of the complex 1. The balanced $[PPh_4]^+$ cations have been omitted for clarity.

Table 4. The selected hydrogen bond parameters ($\text{\AA}$, $^\circ$) for complexes 1–3.

Complex 1			
D-H...A	d(H...A)	d(D...A)	$\angle(\text{DHA})$
O1-H1A...N3	2.116	2.941	175.22
O1-H1B...N5#1	2.317	3.042	138.02
N2-H2...N9#2	1.988	2.820	162.61
N8-H8...N5#3	2.419	3.174	146.94
Complex 2			
O1-H1A...O8#1	2.257	3.029	153.15
O1-H1B...O7#1	2.435	3.119	142.07
O10-H10A...O5#1	2.279	3.033	151.02
O10-H10B...O3#1	2.155	2.984	161.87
O15-H15A...O12#1	2.461	3.022	125.88
O10-H15B...O14#1	2.416	3.022	129.69
Complex 3			
O1-H1A...N8	2.390	2.804	110.57

Symmetry transformations used to generate equivalent atoms: #1 $x, -y+1/2, z+1/2$; #2 $x, -y+1/2, z+1/2$; #3 $x+1, y, z$ (1); #1 $x, -y, z-1/2$ (2).

by five moieties: an anionic Fe complex, one water molecule, one imidazole molecule and two tetraphenylphosphonium cations. The $[\text{Fe}(\text{CN})_5(\text{imidazole})]^{2-}$ anion contains a low-spin Fe^{III} center coordinated by one imidazole unit and five CN units, in which four CN groups occupy the four equatorial positions with the fifth CN group collinearly axial with the imidazole group. The Fe–C bond lengths in a narrow range 1.925(3)–1.958(3) $\text{\AA}$ are slightly shorter than the Fe–N_{imidazole} bond with the value 2.002(2) $\text{\AA}$. The Fe–C $\equiv$ N angles are within the range of 175.4(3)–179.3(3) $^\circ$, indicating the almost linear conformation of these atoms. Under the O–H...N H-bond interactions from the host anion and the co-crystallized water molecules (Table 4), the $[\text{Fe}(\text{CN})_5(\text{imidazole})]^{2-}$ moieties are linked into 1D supramolecular single chain structure (Figure 2).

3. 3. The Crystal Structure of the Complex 2

The cationic tetranuclear structure and the one-dimensional ladder-like double-chain structure formed by

the intermolecular hydrogen bonds for complex 2 are shown in Figures 3 and 4, respectively. The selected important bond parameters for complex 2 are listed in Table 5.

The complex 2 is a neutral tetranuclear cluster comprised by the cationic FeMn_3 unit and an additional disordered ClO_4^- as counter anion. In the FeMn_3 core, $[\text{Fe}(\text{imidazole})(\text{CN})_5]^{2-}$ acting as a *mer-m*₃-coordinating-donor building block is coordinated by three $[\text{Mn}(\text{L})(\text{H}_2\text{O})]^+$ through three cyanide groups and forming a *T*-like arrangement. Each $[\text{Mn}(\text{L})(\text{H}_2\text{O})]^+$ moiety has an elongated octahedral geometry with Jahn-Teller distortion along the $(\text{H}_2\text{O})\text{--Mn--N}_{\text{cyanide}}$ axis, in which the four equatorial positions are coordinated by N_2O_2 unit from the Schiff-base ligand and the two axial ones occupied by one N atom of the bridge cyanide group and one O atom from the H_2O molecule. The average $\text{Mn--N}_{\text{Schiff-base/O}_{\text{Schiff-base}}}$ bond lengths are 1.988(5) $\text{\AA}$ and 1.874(3) $\text{\AA}$, which are obviously shorter than the $\text{Mn--N}_{\text{cyanide}}$ 2.245(5) $\text{\AA}$ and $\text{Mn--O}_{\text{water}}$ 2.298(4) $\text{\AA}$. The $\text{Mn}(1)\text{--N}(1)\text{--C}(1)$ angle (156.5(4) $^\circ$) is slightly bigger than the other two $\text{Mn--N}\equiv\text{C}$ angles with values of 146.4(4) $^\circ$ and 149.2(4) $^\circ$. The intramolecular $\text{Mn}^{\text{III}}\text{--Fe}^{\text{III}}$ distances through bridge-cyanides are very close to each other with values 5.100, 5.100 and 5.154 $\text{\AA}$, respectively, which are slightly longer than the shortest intermo-

Figure 3. The cationic crystal structure of complex 2. All H atoms and the counter ClO_4^- anion have been omitted for clarity.

Table 5. Selected bond lengths (Å) and angles (°) for complexes 2–3.

Complex 2					
Fe(1)–C(1)	1.941(5)	Mn(1)–O(2)	1.889(3)	Mn(2)–O(8)	1.871(3)
Fe(1)–C(2)	1.928(5)	Mn(1)–O(4)	1.863(4)	Mn(2)–N(2)	2.247(4)
Fe(1)–C(3)	1.914(5)	Mn(2)–O(6)	1.873(3)	Mn(2)–N(10)	1.986(4)
Fe(1)–C(4)	1.958(6)	Mn(1)–N(1)	2.253(5)	Mn(2)–N(11)	1.982(4)
Fe(1)–C(5)	1.922(6)	Mn(1)–N(8)	1.996(5)	Mn(2)–O(10)	2.273(3)
Fe(1)–N(6)	1.986(4)	Mn(1)–N(9)	1.980(5)	Mn(1)–O(1)	2.336(4)
Mn(1)–N(1)–C(1)	156.1(4)	Mn(2)–N(2)–C(2)	146.4(4)		
Mn(3)–N(3)–C(3)	149.1(4)	Fe(1)–C(1)–N(1)	171.1(5)		
Fe(1)–C(2)–N(2)	175.3(5)	Fe(1)–C(3)–N(3)	175.9(5)		
Fe(1)–C(4)–N(4)	175.3(5)	Fe(1)–C(5)–N(5)	176.5(5)		
C(1)–Fe(1)–C(2)	172.0(2)	N(3)–Mn(3)–O(15)	175.7(2)		
N(2)–Mn(2)–O(10)	170.6(1)	N(1)–Mn(1)–O(1)	174.3(1)		
Complex 3					
Fe(1)–C(1)	1.936(5)	Fe(2)–C(7)	1.946(6)	Mn(1)–N(1)	2.199(5)
Fe(1)–C(2)	1.941(7)	Fe(2)–C(8)	1.939(6)	Mn(1)–N(6)	2.220(5)
Fe(1)–C(3)	1.958(6)	Fe(2)–C(9)	1.940(6)	Mn(1)–N(11)	2.251(5)
Fe(1)–N(4)	1.958(6)	Fe(2)–N(9)	1.940(6)	Mn(1)–N(12)	2.294(4)
Mn(1)–N(13)	2.299(4)	Mn(1)–N(14)	2.242(5)		
Fe(1)–C(1)–N(1)	179.3(5)	Fe(2)–C(7)–N(6)	177.1(5)		
Fe(1)–C(2)–N(2)	178.9(6)	Fe(2)–C(8)–N(7)	179.8(6)		
Fe(1)–C(3)–N(3)	173.2(9)	Fe(2)–C(9)–N(8)	176.5(11)		
Mn(1)–N(1)–C(1)	161.7(5)	Mn(1)–N(12)–C(16)	112.0(4)		
Mn(1)–N(6)–C(7)	152.6(4)	Mn(1)–N(12)–C(17)	110.8(4)		
Mn(1)–N(11)–C(13)	123.9(5)	Mn(1)–N(13)–C(18)	115.1(5)		
Mn(1)–N(11)–C(15)	116.6(4)	Mn(1)–N(13)–C(19)	109.6(3)

Figure 4. One-dimensional double-chain structure of complex 2 formed by intermolecular hydrogen-bond interactions. All the H atoms except those used to form hydrogen bonds and the balance ClO_4^- have been omitted for clarity.

lecular metal-metal separation. Because of the excellent encapsulation ability of the O_4 compartment for the water molecule, one-dimensional ladder-like double chain structure is formed under the help of the intermolecular H-bond interactions (Table 3) between the O_{H_2O} atoms and the O atoms of the Schiff-base ligand.

3. 4. The Crystal Structure of the Complex 3

The asymmetry binuclear unit and 1D neutral chain structure of complex **3** is presented in Figure 5. The important bond parameters are given in Table 5. As can be found, complex **3** possesses one-dimensional neutral single chain structure comprising of the repeating $[-NC-Fe(imidazole)(CN)_3-CN-Mn(MAC)-]$ units. In this complex, each $[Fe(imidazole)(CN)_5]^{2-}$ unit, functioning as bidentate ligand through its two cyanide groups in *trans* position, connects the Mn(II) ions of two independent macrocyclic manganese units. Similar to that in compounds **1** and **2**, the coordination geometry of the Fe atom is also a slightly distorted octahedral. As listed in Table 5, the bond angle of $Fe-C\equiv N$ in the range of $171.1(5)$ – $176.5(5)^\circ$ clearly indicates that the three atoms are in a good linear configuration. The Mn^{II} ion displays the hepta-

ta-coordinates mode and involved in a pentagonal-bipyramidal geometry with the macrocyclic ligand forming the equatorial plane. The five equatorial positions are occupied by N_5 unit from the macrocyclic ligand, while the axial positions are occupied by two N atoms of the bridging cyanide groups. The $Mn-N_{MAC}$ distances within the range 2.196 – 2.299 Å are with no conspicuous with the $Mn-N_{cyanide}$ bond lengths ($2.199(5)$ and $2.220(5)$ Å), indicating the only slightly distorted pentagonal-bipyramidal geometry of the Mn(II) ion. With comparison to the $Fe-C\equiv N$ angle distributed in a very narrow range of $179.3(5)$ – $177.1(5)^\circ$, the bridging cyanide ligands coordinated to the Mn(II) ions in a bent fashion with the $Mn-N\equiv C$ angles are $152.6(4)$ and $161.7(5)^\circ$, respectively.

3. 5. The Magnetic Properties of Complexes 2 and 3

The temperature dependences of the $c_m T$ product per $Fe^{III}Mn^{III}_3$ and $Fe^{III}Mn^{II}$ unit for **2** and **3** measured from 2 to 300 K under an applied magnetic field of 2000 Oe are shown in Figures 6 and 7. The $c_m T$ value at room temperature is 9.11 emu K mol $^{-1}$ ($\mu_{eff} = 8.57$ BM) for **2** and 4.33 emu K mol $^{-1}$ ($\mu_{eff} = 5.91$ BM) for **3**, which are slightly

Figure 5. Asymmetry neutral unit and 1D neutral chain structure of complex **3**. All the hydrogen atoms and solvent molecules have been omitted for clarity.

lower than the spin only value of $9.375/4.75 \text{ emu K mol}^{-1}$ for uncoupled three high spin Mn(III) ($S = 2$)/one high spin Mn(II) ($S = 5/2$) and one low spin Fe(III) ($S = 1/2$) based on $g = 2.00$, respectively. For these two complexes, the $c_m T$ values maintains nearly constant until the temperature lowering to 20 K for 2 and 50 K for 3. After that, the $c_m T$ value for complex 2 starts to increase smoothly and reaches its highest value $10.12 \text{ emu K mol}^{-1}$, and then decreases rapidly to the lowest value about $0.87 \text{ emu K mol}^{-1}$ at 2 K. The suddenly decrease for the $c_m T$ value in the low temperature range can maybe attributed to the comparable strong intermolecular H-bond interaction and/or the zero field splitting of the Mn(III) ion. Different from that for complex 2, the $c_m T$ value of complex 3 presents the obvious decreasing tendency from 50 K, and attains its minimum value $2.19 \text{ emu K mol}^{-1}$ at 2 K, implying the different coupling nature in these two complexes. The magnetic susceptibilities of 2 and 3 conform well to Curie-Weiss law and give the positive Weiss constant $q = 1.87 \text{ K}$, Curie constant $C = 8.90 \text{ emu K mol}^{-1}$ for 2 and negative $q = -1.90 \text{ K}$, $C = 4.54 \text{ emu K mol}^{-1}$ for 3. On the basis of the Weiss constant and with the combination of change tendency of $c_m T$ - T curves, the overall ferromagnetic magnetic coupling between Fe(III) and Mn(III) ions in complex 2 and antiferromagnetic coupling between Fe(III) and Mn(II) ion in 3 can be concluded.

In view of the situation that the three Mn-N≡C-Fe bridges are structurally independent and the coordination environment of the three Mn(III) ions are not completely same to each other with the Mn-N≡C angles $146.4(4)$ – $156.1(4)^\circ$ and the Mn-N_{CN} bond lengths $1.980(5)$ – $2.253(5) \text{ Å}$, the simulation of the magnetic susceptibility for this compound should be based on three different J values ($J_1 \neq J_2 \neq J_3$), where the three J values represent the Mn(1)...Fe(1), Mn(2)...Fe(1) and Mn(3)...Fe(1) interactions through cyanide bridges, respectively. On the other hand, according to the method successfully employed to simu-

late the magnetic susceptibilities of 1D chain compound with alternating spins $1/2$ and 2 ,^{30b} the one-dimensional chain structure of the complex 3 can be considered as isotropic Heisenberg chain containing alternating spins $1/2$ and $5/2$ with two antiferromagnetic exchange interactions J_1 and J_2 . In this case, the magnetic susceptibility of this complex can be calculated rationally based on a closed ring cluster model consisting of five $1/2$ – $5/2$ spin pairs,

Figure 7. Temperature dependence of $c_m T$ of complex 3 (the solid line represents the best fit based on the parameters discussed in the text). Inset: Field dependence of magnetization at 2 K (the dotted line is the Brillouin curve for antiferromagnetically coupled Fe(III) and Mn(II) ions with $g = 2.0$).

Scheme 4.

Evaluation of the exchange coupling between the iron(III) ion and manganese(III/II) ions bridged by cyanide group in complexes 2 and 3 are carried out by MAGPACK program.⁴⁷ The best-fit parameters obtained are $J_1 = 1.12$, $J_2 = 1.65$, $J_3 = 0.91 \text{ cm}^{-1}$, $D = -1.81 \text{ cm}^{-1}$, $g = 2.02$, R

Figure 6. Left: The $c_m T$ - T (the solid line represents the best fit based on the parameters discussed in the text) and $c_m T$ curve for complex 2. Right: The field-dependent magnetization for complex 2.

Scheme 4. The magnetic simulation model for the complex **3**.

$= \Sigma(c_{\text{obsd}}T - c_{\text{calcd}}T)^2 / \Sigma(c_{\text{obsd}}T)^2 = 1.61 \times 10^{-5}$ for complex **2** and $J_1 = -1.34$, $J_2 = -0.54(1) \text{ cm}^{-1}$, $g = 1.99$, $R = 3.01 \times 10^{-5}$ for complex **3**, respectively. All the theoretical fitting results are comparable to those found in the previously reported cyanide-bridged $\text{Fe}^{\text{III}}\text{-Mn}^{\text{III/II}}$ complexes.^{42–44, 48} The field-dependent magnetizations measured up to 50 kOe at 2 K for complexes **2** and **3** are shown in Figure 6 and the inset of Figure 7, respectively. The field-dependent magnetization curve for complex **2** has a sigmoid shape, implying maybe the metamagnetic behavior: The magnetization first increases slowly with increasing magnetic field until 20 kOe because of the relatively strong intermolecular hydrogen bond interaction, then increases abruptly for a phase transition at about 20 kOe, and finally attains the highest value about $7.45 N\beta$, which is slightly higher than the saturated value for three $\text{Mn}(\text{III})$ ion ($S = 2$) and one low spin $\text{Fe}(\text{III})$ ion ($S = 1/2$). For complex **3**, the magnetization quickly increases with the field increasing until about 15 kOe, then increases smoothly up to about $3.9 N\beta$ until 50 kOe. This data is very close to the saturated value of $4.0 N\beta$ but obviously lower than the value of uncoupled low spin $\text{Fe}(\text{III})$ and $\text{Mn}(\text{II})$ based on $g = 2.0$, confirming again the overall antiferromagnetic coupling interaction between $\text{Fe}(\text{III})$ and $\text{Mn}(\text{II})$ ions bridged by cyanide group.

4. Conclusion

In summary, two new heterobimetallic cyanide-bridged complexes have been prepared with pentacyanoiron(III) as building block and manganese(III/II) compounds as the counterpart assemble segment. The single crystal X-ray analysis revealed the cationic tetranuclear FeMn_3 entity or one-dimensional infinite chain structure, respectively. For the polynuclear cluster, it can be self-complementary through coordinated aqua ligand from one complex and the free O_4 compartment from the neighboring complex, therefore giving interesting supramolecular

one-dimensional ladders. The experimental and theoretical investigation on their magnetic properties disclose the ferro- or antiferromagnetic coupling in cyanide-bridged $\text{Fe}^{\text{III}}\text{-Mn}^{\text{III}}$ or $\text{Fe}^{\text{III}}\text{-Mn}^{\text{II}}$ units, respectively. The present results can further enrich the pentacyanometallate-based molecule magnetic system, which is helpful for fully discover the magneto-structural relation from the molecule magnetism.

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Povzetek

V tem prispevku je na osnovi strukturno potrjenega pentacianidometalata $(\text{PPh}_4)_2[\text{Fe}(\text{CN})_5(\text{imidazol})] \cdot (\text{imidazol}) \cdot \text{H}_2\text{O}$ (**1**) in manganovih spojin $[\text{Mn}(\text{L})(\text{H}_2\text{O})_2]\text{ClO}_4$ ($\text{L} = \text{N,N}$ -etilenbis(3-metoksisalicilideniminat) in $[\text{Mn}(\text{MAC})(\text{H}_2\text{O})\text{Cl}]\text{ClO}_4$ ($\text{MAC} = 2,13$ -dimetil-3,6,9,12,18-pentaazabiklo-[12.3.1]oktadeka-1(18),2,12,14,16-pentaen) opisana sinteza dveh novih $\text{Fe}^{\text{III}}\text{-Mn}^{\text{III/II}}$ kompleksov s cianidnim mostom, $\{[\text{Mn}(\text{L})(\text{H}_2\text{O})]_3[\text{Fe}(\text{CN})_5(\text{imidazol})]\}(\text{ClO}_4)$ (**2**) in $\{[\text{Mn}(\text{MAC})][\text{Fe}(\text{CN})_5(\text{imidazol})] \cdot \text{CH}_3\text{OH}\}_n$ (**3**), njihova karakterizacija z elementno analizo, IR spektroskopijo in rentgensko strukturno analizo. Rentgenska analiza na monokristalu je pokazala, da je spojina **2** zgrajena iz tetranuklearnih enot FeMn_3 , ki se z močnimi vodikovimi vezmi povezujejo v supramolekularne 1D dvojne verige v obliki lestve, medtem ko spojino **3** sestavljajo nevtralne enodimenzionalne enojne verige. Magnetne meritve so pokazale feromagnetno sklopitev med $\text{Fe}^{\text{III}}\text{-Mn}^{\text{III}}$ enotami in anti-feromagnetno sklopitev med $\text{Fe}^{\text{III}}\text{-Mn}^{\text{II}}$ enotami preko mostovnih cianidnih skupin v spojinah **2** in **3**.

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