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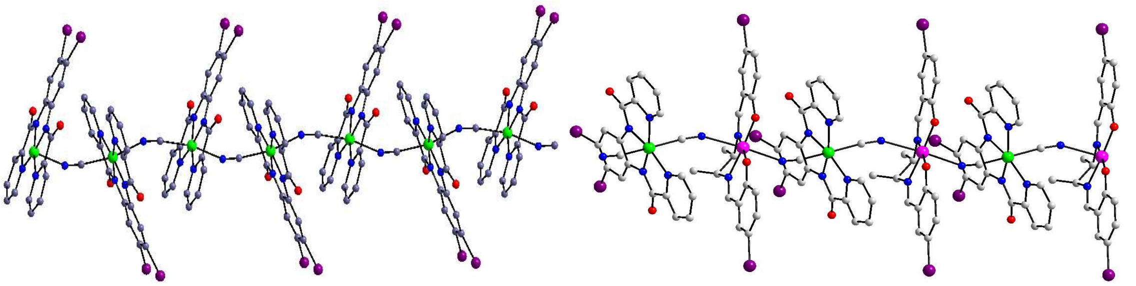
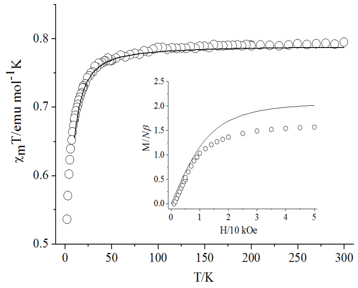
Graphical abstract:

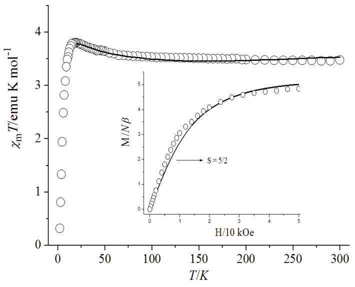
A New Series of Cyanide-Bridged Hetrobimetallic Fe^{III}-Fe^{III}/Mn^{III}/Cu^{II} One-dimensional Complexes: Synthesis, Crystal Structures, and Magnetic Properties

Daopeng Zhang,[a,b] Shuping Zhuo,[a,*] Ping Wang,[a] Xia Chen,[a] and Jianzhuang Jiang[b,*]

Four new cyanide-bridged Fe^{III}-Fe^{III}/Mn^{III}/Cu^{II} one-dimensional complexes have been assembled with $K[Fe(bpdBrb)(CN)_2]\}\cdot 2H_2O$(**1**) as building block, structurally characterized and magnetically investigated.







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ARTICLE TYPE

A New Series of Cyanide-Bridged Hetrobimetallic Fe^{III}-Fe^{III}/Mn^{III}/Cu^{II} One-Dimensional Complexes: Synthesis, Crystal Structures, and Magnetic Properties

Daopeng Zhang,[a,b] Shuping Zhuo,[a,*] Ping Wang,[a] Xia Chen,[a] and Jianzhuang Jiang[b,*]

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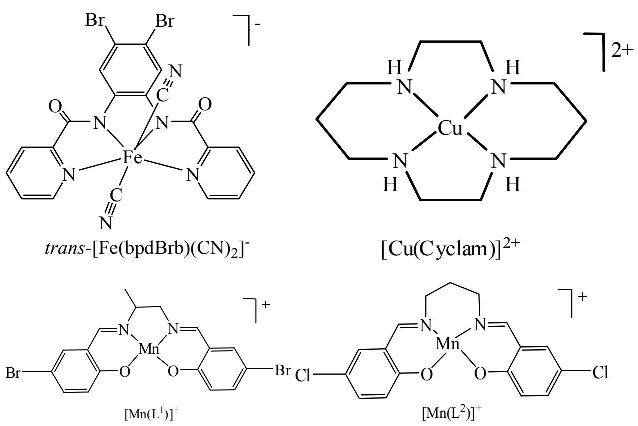
The *trans*-dicyanide-containing precursor K[Fe(bpdBrb)$(CN)_2$]}·$2H_2O$(**1**) (bpdBrb^{2-} = 1,2-bis(pyridine-2-carboxamido)-4,5-dibromobenzenate) and four transition metal compounds Fe^{III}, Mn^{III} or Cu^{II} have been employed as building blocks to assemble cyanide-bridged systems, resulting in a series of new cyanide-bridged single chain complexes $[Fe(bpdBrb)(CN)]_n$·nCH_3OH (**2**), $\{[Mn(L^1)][Fe(bpdBrb)(CN)_2]\}_n$·$nCH_3CN$ (**3**), $\{[Mn(L^2)][Fe(bpdBrb)(CN)_2]\}_n$·$2nH_2O$ (**4**) and $\{[Cu(cyclam)][Fe(bpdBrb)(CN)_2]\ ClO_4\}_n$·$nCH_3OH$ (**5**) (L^1 = 5-Brsalpn and L^2 = 5-Clsaltn). Single crystal X-ray diffraction analysis reveals the rare one-dimensional "shish-kebab" neutral structure of complex **2** with bpdBrb^{2-} as equatorial ligand and single cyanide ligands as axial bridges. The other three cyanide-bridged complexes can be structurally characterized as the neutral one-dimensional chains (**2** and **3**) consisting of alternating units of $[Mn(L)]^+$ (L = L^1 or L^2) and $[Fe(bpdBrb)(CN)_2]^-$ and cationic one-dimensional single chain (**4**) consisting of the repeating units $\{NC\text{-}[Fe(bpdBrb)]\text{-}CN\text{-}Cu(cyclam)\}^+$ with free ClO_4^- as counter ainion, respectively. Investigation of the magnetic properties of the four 1D chain complexes reveals the antiferromagnetic magnetic coupling between neighbouring low spin Fe(III) ions in complex **2** and ferromagnetic interaction between the cyanide-bridged Fe(III)-Mn(III)/Cu(II) ions in complexes **3**-**5**, respectively. By employing infinite chain models or MAGPACK program, the magnetic susceptibilities of these complexes were simulated, leading to the magnetic coupling constants J = -1.98 (2) cm^{-1} for **2**, J_1 = 0.56(1), J_2 = 0.45(2) cm^{-1} for **3**, J_1 = 0.59(3), J_2 = 0.43(8) cm^{-1} for **4**, and J = 1.77(5) cm^{-1} for **5**.

Introduction

Due to their fundamental importance and potential applications in magnetic devices,[1-4] molecule-based magnetic materials have been explored intensively in the past three decades. In view of the excellent magnetic transferring ability of cyanide group and their readily controlled and predicted topology of its bridged structures, cyanide-bridged magnetic complexes have always been the focus in the molecular magnetism field. Up to now, about twenty cyanide-containing precursors with or without peripheral organic ligands have been employed to synthesize cyanide-bridged magnetic compounds with diverse molecular topological structures and interesting magnetic properties such as high-T_c magnets,[5,6] photomagnetic materials,[7-9] spin crossover materials,[10-12] chiral magnets[13-17] and single-molecule magnets (SMMs)[18-20] as well as single-chain magnets (SCMs).[21-23]

Very recently, with the aim of clearly elucidating magneto-structural correlation and preparing interesting molecular materials such as SMMs and SCMs, low-dimensional cyanide-bridged complexes have attracted much attention.[24-26] To synthesize low-dimensional cyanide-bridged complexes with expected molecular structure, several factors including the number and position of cyanide group, number and nature of charge of cyanide-containing building block, and steric effect of reactants must be taken into account. With this idea in mind, we have developed a series of cyanide building blocks containing relatively large equatorial in-plane ligands and two *trans* cyanide groups so as to prepare new low-dimensional cyanide-bridged magnetic complexes.[27-29] To find new molecular materials with interesting magnetic properties and also to further enrich the low-dimensional cyanide-bridged family, we investigated the reactions of another *trans*-dicyanide precursor with some paramagnetic segments with different structures (Scheme 1) and obtained a rare "shish-kebab" mono-metallic and three heterobimetallic cyanide-bridged one-dimensional single chain complexes. It should be noted that complex **2** is the first example of low spin iron(III) chain containing alternating iron sites and alternating bridging ligand. The synthesis, crystal structures, and magnetic properties for the four 1D complexes with the formula $[Fe(bpdBrb)(CN)]_n$·nCH_3OH (**2**), $\{[Mn(L^1)][Fe(bpdBrb)(CN)_2]\}_n$·$nCH_3CN$ (**3**), $\{[Mn(L^2)][Fe(bpdBrb)(CN)_2]\}_n$·$2nH_2O$ (**4**) and $\{[Cu(cyclam)][Fe(bpdBrb)(CN)_2][ClO_4]\}_n$·$nCH_3OH$ (**5**), as well as the structure of the cyanide precursor K[Fe(bpdBrb)$(CN)_2$]} $2H_2O$(**1**), will be described in this paper.



Scheme 1. The starting materials used to prepare the complexes.

Experimental Section

General measurements. Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementary Vario El. The infrared spectroscopy (KBr pellets) was performed on a Magna-IR 750 spectrophotometer in the 4000-400 cm^{-1} region. Variable-temperature magnetic susceptibility and field dependence magnetization measurements were performed on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

Synthesis. All the reactions were carried out in air and all chemicals and solvents used were reagent grade without further purification. The cyanide precursor was synthesized by a modified method for its analogue $K[Fe^{III}(bpb)(CN)_2]$ [bpb^{2-} = 1,2-bis(pyridine-2-carboxamido)benzenate] with 4,5-dibromo-*o*-phenylenediamine instead of phenylenediamine.[30] The two Schiff-base manganese compounds were prepared by the reported method.[31]

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

Synthesis of the precursor $K[Fe^{III}(bpdBrb)(CN)_2]\cdot CH_3OH$ (1). To a solution of H_2bpdBrb (474 mg, 1.0 mmol) in methanol (20 mL) was slowly added $FeCl_3$ (106.5 mg, 1.0 mmol). The mixture was refluxed for about 3 h. KCN (650 mg, 10 mmol) was added to the solution formed and then the suspension was stirred until the colour of the mixture changed into dark green with the temperature maintaining at 60°C. After removing the solvent by a rotor evaporator under the reduced pressure, the solid obtained was dissolved in DMF, and then the undisolved excess KCN was filtered. The filtrate was concentrated under reduced pressure, and excess amount of ether was added to precipitate the dark-green solid, which was collected by filtration, washed with ether, and dried under vacuum. Yield: 432 mg, 66%. Anal. Calcd. for $C_{20}H_{14}Br_2FeKN_6O_4$: C, 36.56; H, 2.15; N, 12.79. Found: C, 36.47; H, 2.01; N, 12.911. Main IR bands (cm^{-1}): 2150 (s, νC≡N).

Synthesis of complexes 2 and 5. These two complexes were obtained by the baker reaction. To a solution of $Fe(bpdBrb)(H_2O)Cl$ (58.3 mg, 0.10 mmol) or $[Cu(cyclam)][ClO_4]_2$ (48.3 mg, 0.10 mmol) in methanol (10 mL), $K[Fe(bpdBrb)(CN)_2]\cdot CH_3OH$ (65.7 mg, 0.10 mmol) dissolved in methanol/water (4:1, v:v) (10 mL) was carefully added. The resulting mixture was filtered at once and the filtrate kept undisturbed at room temperature. After one week, dark-brown block crystals were collected by filtration.

Complex **2**: Yield 48.5 mg, 41.2%. Anal. Calcd. for $C_{20}H_{14}Br_2FeN_5O_3$: C, 40.85; H, 2.40; N, 11.91. Found: C, 40.68; H, 2.31; N, 12.10. Main IR bands (cm^{-1}): 2120 (s, νC≡N), 1618, 1625 (vs, νC=N).

Complex **5**: Yield: 58.1 mg, 59.5%. Anal. Calcd. for $C_{31}H_{38}Br_2ClCuFeN_{10}O_7$: C, 38.10; H, 3.92; N, 14.33. Found: C, 37.95; H, 3.81; N, 14.50. Main IR bands (cm^{-1}): 2118 (s, νC≡N), 1620, 1626 (vs, νC=N), 1100 (vs, νCl=O).

Synthesis of complexes 3 and 4:

These two complexes were prepared by using a diffusion method. A solution containing $K[Fe^{III}(bpdBrb)(CN)_2]\cdot CH_3OH$ (65.7 mg, 0.10 mmol) dissolved in DMF/ CH_3OH (2:1, v:v) 5ml was laid in the bottom of a tube, upon which a mixture of DMF and CH_3OH with a ratio of 4:1 was carefully added. Then, the methanol/ acetonitrile solution containing the corresponding stoichiometric Schiff-base manganese compound was carefully added to the top of the mixed solvent layer. Single crystals suitable for X-ray diffraction were obtained about one week later, which were then collected by filtration and dried in air.

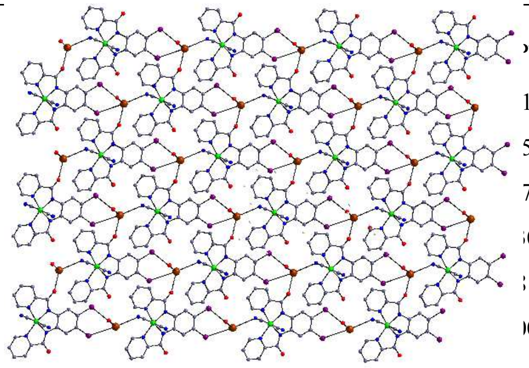
Complex **3**: Yield: 73 mg, 65.8%. Anal. Calcd. for $C_{37}H_{27}Br_4FeMnN_8O_6$: C, 40.03; H, 2.45; N, 10.09. Found: C, 39.87; H, 2.32; N, 10.22. Main IR bands (cm^{-1}): 2115 (s, νC≡N), 1620, 1630 (vs, νC=N).

Complex **4**: Yield: 62.6 mg, 61%. Anal. Calcd. for $C_{35}H_{33}Cl_2FeMnN_9O_{8.5}$: C, 45.60; H, 2.65; N, 12.27. Found: C, 45.51; H, 2.53; N, 12.39. Main IR bands (cm^{-1}): 2120 (s, νC≡N), 1618, 1627 (vs, νC=N).

X-ray data collection and structure refinement. Data were collected on a Oxford Diffraction Gemini E diffractometer with Mo *Kα* radiation (λ = 0.71073 Å) 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.[32] Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were assigned isotropic displacement coefficients U(H) =1.2U(C) or 1.5U(C) and their coordinates were allowed to ride on their respective carbons using SHELXL97 except some of the H atoms of the solvent molecules. For these H atoms, refine was tropically with fixed U values and the DFIX command was used to fix the bond lengths. CCDC 1000032-1000036 for complexes **1-5** 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 crystal parameters, data collection, and refinement are summarized in Table 1.

Table 1. Crystallographic data for complexes **1-5**.

	1	2	3
chemical formula	$C_{20}H_{14}Br_2FeKN_6O_4$	$C_{20}H_{14}Br_2FeN_5O_3$	$C_{37}H_{27}Br_4FeMnN_8O_6$
Fw	657.14	588.03	1110.06
crystal system	Triclinic	Orthorhombic	Triclinic



			P1̄
			12(2)
			50(3)
			77(4)
			08(3)
			16(4)
			04(3)
V/Å^3	1151.1(5)	2162.2(9)	2001.2(7)
Z	2	4	2
F(000)	646	1156	1084
GOF^a	1.071	1.060	1.030
$R_1{}^b[I>2\sigma(I)]$	0.0462	0.0703	0.0478
$wR_2{}^c$(all data)	0.0611	0.1847	0.1383

Continued:

	4	5
chemical formula	$C_{39}H_{27}Br_2Cl_2FeMnN_9O_4$	$C_{31}H_{38}Br_2ClCuFeN_{10}O_7$
Fw	1027.21	977.37
crystal system	Triclinic	Triclinic
Space group	P1̄	P1̄
a/Å	10.3171(7)	10.8178(14)
b/Å	11.5913(7)	13.1598(17)
c/Å	17.7730(16)	14.3844(18)
α/deg	102.520(10)	78.246(2)
β/deg	102.070(10)	71.433(2)
γ/deg	104.978(10)	86.186(2)
V/Å^3	1923.6(2)	1900.5(4)
Z	2	1
F(000)	1568	908
GOF^a	1.054	1.012
$R_1{}^b[I>2\sigma(I)]$	0.0718	0.0734
$wR_2{}^c$(all data)	0.1745	0.2354

[a] $[\sum w(|Fo\text{-}Fc|)^2/(N_{obs} - N_{para})]^{1/2}$. [b] $\sum |Fo|^2 - |Fc|^2/\sum Fo^2$. [c] $[\sum w(|Fo|^2 - |Fc|^2)^2/\sum w\, Fo^2]^{1/2}$; $w = 1/[\sigma^2(Fo) + (0.020Fo)^2 + 1.000]$–$Fo$.

Results and discussions

Synthesis and general characterization

A serials of recent works[27-29] have proven that *trans*-dicyanidoiron(III) $[Fe(L')(CN)_2]^-$ (L' = bpb and its analogues) are good building block for synthesizing cyanide-bridged complexes. The relative large planar equatorial pyridinecarboxamido ligand can not only effectively lower the dimensionality of the complex formed, but also weaken the intermolecular magnetic interactions.

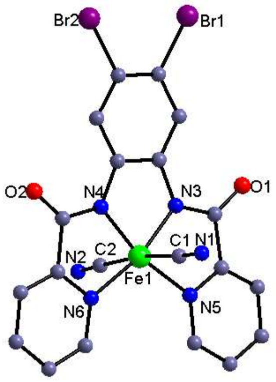
The reaction between **1** and [Fe(bpdBrb)]Cl with 1:1 molar ratio led to the isolation of an interesting 1D monometallic cyanide-bridged complex. It is worth noting that among ion(III) polymers, structurally characterized chain complexes are with alternating iron sites are very rare.[33-35] To our best of the knowledge, there has no report on the low spin ion(III) chain containing alternating iron sites and also alternating bridging ligands. Two neutral 1D complexes were obtained with $K[Fe(bpdBrb)(CN)_2]$ as building block and $[Mn(L^1)(H_2O)_2]ClO_4$ or $[Mn(L^2)(H_2O)_2]ClO_4$ as assemble segments, whose structures are different from the products obtained by the reactions of other analogues cyanide precursors with the above two manganese compounds,[28c] indicating that the cyanide precursor play an important role on influencing the structure of the complexes formed. Different from complexes **2-4**, the cyanide-bridged Fe(III)-Cu(II) complex **5** is structurally characterized as cationic single chain with the positive charge balanced by ClO_4^- anion.

All the cyanide-bridged complexes and the cyanide precursor have been characterized by IR spectra. In the IR spectrum of compound **1**, the broad absorption locate at about 2150 cm^{-1} was assigned to the terminal cyanide group. For complexes **2-5**, only one broad peak due to the bridging cyanide groups in the range of 2115-2120 cm^{-1} was observed in their IR spectra, indicating the existence of only bridging cyanide ligands in these compounds. In addition, a strong broad peak observed at ca. 1100 cm^{-1} in the IR spectra of **5** suggests the presence of ClO_4^- anions in this complex.

Crystal Structure of Complexes 1-5.

The crystal structure of complex **1** and its two-dimensional structure formed by K-O, K-Br and K-N interactions are shown in Figure 1. Compound **1** possessing a low-spin central Fe(III) ion contains octahedral mono-anion $[Fe(bpdBrb)(CN)_2]^-$. The Fe(III) ion is six-coordinate, with four equatorial nitrogen atoms and two carbon atoms of two cyanide groups with a *trans* disposition. The bond lengths of Fe-C are 1.972(7) and 1.978(7) Å, respectively, which are slightly longer than the Fe-N bond lengths, indicating a slightly distorted octa-coordination sphere of the Fe(III) ion. The Fe1-C1≡N1 and Fe1-C2≡N2 angles are nearly linear with the values very close to 180°.

The temperature dependence of magnetic susceptibility for compound **1** measured in the range of 2-300 K under an external magnetic field of 2000 Oe is illustrated in Figure S1(Electronic Supplementary Information (ESI)). The $\chi_M T$ value at room temperature is 0.51 emu K mol^{-1}, higher than the low-spin Fe(III) value of 0.375 K mol^{-1}, which can be attributed to the spin-orbital coupling. With the temperature lowering, the $\chi_M T$ value decreases with a very low speed up to about 60K, and then decreases with a high speed and reaches the value of about 0.2 emu K mol^{-1} at 2 K.



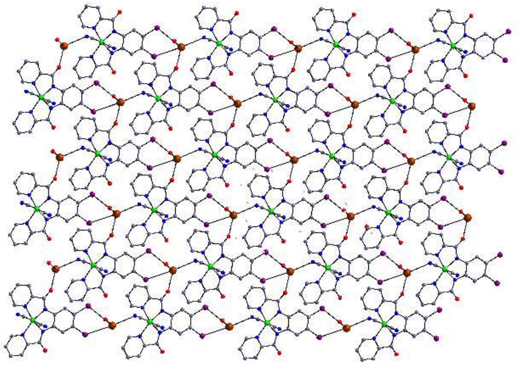


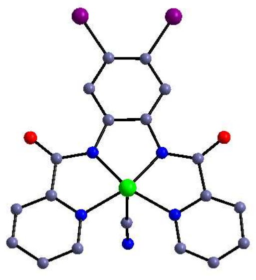
Figure 1. The anionic structure of compound **1**(top) and its two-dimensional structure formed by K-O, K-Br and K-N bonds (bottom). The solvent methanol molecule and all the hydrogen atoms have been omitted for clarity.

Selected bond lengths and angles for complexes **2**-**5** are given in Table 2. The asymmetric unit and the neutral one-dimensional structure for complex **2** are depicted in Figure 2. As can be seen, complex **2** possesses a perfect one dimensional neutral "shish-kebab" structure comprised of repeating [Fe(bpdBrb)(CN)] units. The Fe atom is coordinated by the four N atoms of cyanide-containing precursor located in the equatorial plane and the C and N atoms of the cyanide ligands in *trans* positions. The Fe-N$_{\text{bpdBrb}}$ bond length is in the range of 1.902(8)-2.032(7) Å, while the Fe-C$_{\text{cyanide}}$ and Fe-N$_{\text{cyanide}}$ bond lengths are 2.121(10) and 2.171(11) Å, respectively, clearly indicting the axially elongated distorted octahedron around the Fe atom.

Table 2. Selected bond lengths (Å) and angles ($^{\circ}$) for complexes **1** and **2.**

	1		2
Fe1-C1	1.978(7)	Fe1-C1	2.121(10)
Fe1-C2	1.972(7)	Fe1-N1#1	2.171(11)
Fe1-N3	1.891(5)	Fe1-N2	1.902(8)
Fe1-N4	1.894(5)	Fe1-N3	1.910(7)
Fe1-N5	2.013(5)	Fe1-N4	2.032(7)
Fe1-N6	2.008(5)	Fe1-N5	2.022(8)
N(1)-C(1)-Fe(1)	176.0(5)		
N(2)-C(2)-Fe(1)	178.4(6)	C(1)-N(1)-Fe(1)#2	158.4(10)

Symmetry transformations used to generate equivalent atoms for complex **2**: #1 -x+1, y+1/2, -z+1/2 #2 -x+1, y-1/2, -z+1/2.



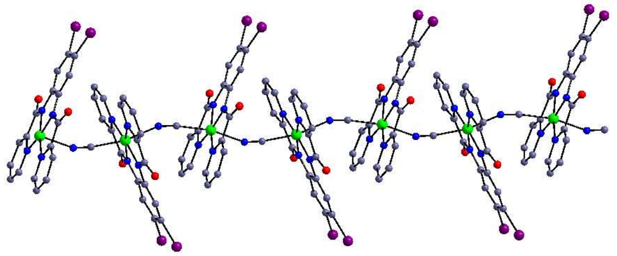


Figure 2. The asymmetric unit and the neutral one-dimensional structure of complex **2**. All the H atoms and the solvent molecules were omitted for clarity.

For complexes **3** and **4**, their asymmetry unit and one-dimensional cationic chain structures are shown in Figures 3 and 4, respectively.

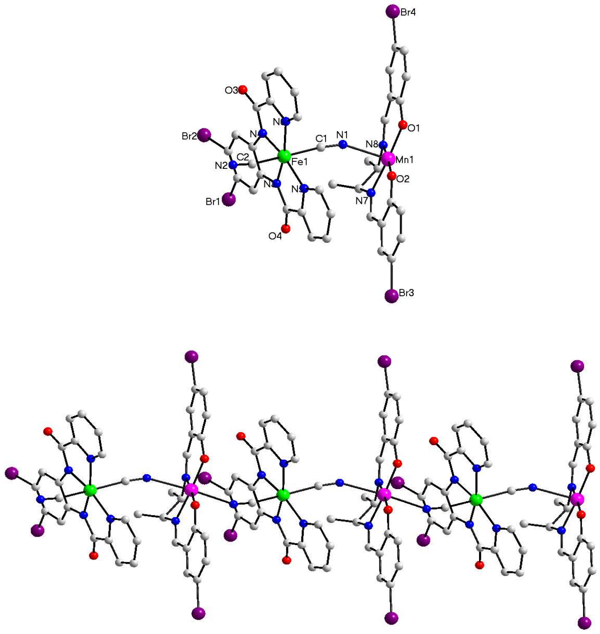


Figure 3. The asymmetry unit and one-dimensional chain structure of complex **3**. All the hydrogen atoms and solvent water molecules have been omitted for clarity.

X-ray diffraction analyses show that the complexes **3** and **4** are isostructural and possess a neutral chain structure consisting of alternating Fe(III) and Mn(III) ions. In the chains, each *trans*-[Fe(bpdBrb)(CN)$_2$]$^-$ connects two [Mn(L)]$^+$ with two *trans*-cyanide groups, and in turn each *trans*-[Mn(L)]$^+$ unit links two *trans*-[Fe(bpdBrb)(CN)$_2$]$^-$ building blocks, in which the [Fe(bpdBrb)(CN)$_2$] and [Mn(L)]$^+$ groups are disposed parallel to each other. Similar to that in compound **1**, the coordination sphere of the Fe(III) ion is also a distorted octahedron. The Fe-C≡N bond angles in these two complexes are very close to each other, with the value of ca. 174° indicating a good linear configuration of these three atoms.

The Mn(III) ion in **3** and **4** is six-coordinate, forming a slightly distorted octahedral geometry, in which the four equatorial positions are occupied by the N$_2$O$_2$ unit coming from the Schiff-base ligand and the two axial positions coordinated by the two N atoms of the cyanide groups. As tabulated in Table 3, the Mn-N$_{\text{cyanide}}$ bond lengths are obvious longer than the Mn-N$_{\text{Schiff-base}}$ bond length, which gives rise to an elongated octahedral geometry around the Mn(III), with the Jahn-Teller axis lying along the z direction, i.e. the $N_{cyanide}$–Mn–$N_{cyanide}$ axis. The bridging Mn–N≡C bond angles lie in the small range 146.8(3)-154.6(4), indicating that these three atoms deviate markedly from a linear configuration. The intra-chain Fe^{III}-Mn^{III} separation through bridging cyanide(s) is 5.243 Å in **3** and 5.215 Å in **4**, while the shortest inter-chain metal-metal distances are 7.636 Å in **3** and 8.309 Å in **4**.

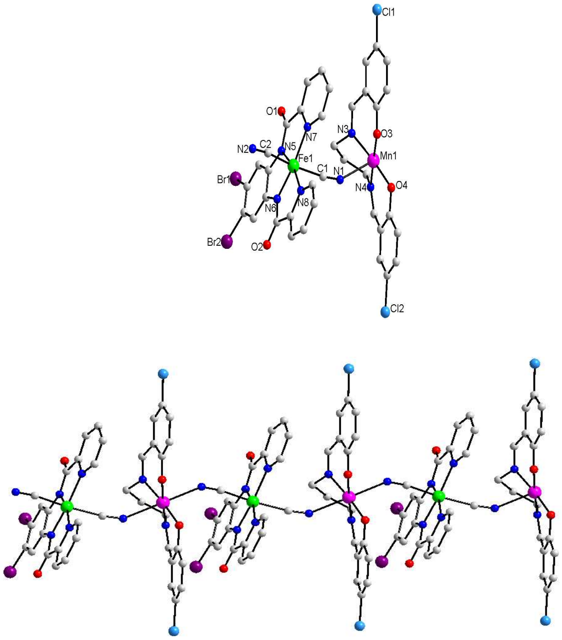
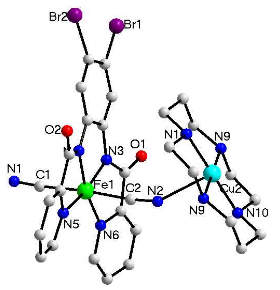


Figure 4. The asymmetry unit and one-dimensional structure of complex **4**. All the hydrogen atoms and solvent water molecules have been omitted for clarity.

Different from the complexes **2**-**4**, complex **5** possesses cationic one dimensional structure comprised of repeating [-NC-Fe(bpdBrb)-CN-Cu(cyclam)-]$^+$ units (Figure 5) with the positive charge balanced by ClO_4^- anions. The coordination sphere for both of the Fe(III) and Cu(II) ions is octahedral. The Cu(II) ion is coordinated by a N_6 unit, in which the four equatorial positions are occupied by the four N atoms of the cyclam ligand, and the other two axial ones come from the N atoms of the bridging cyanide groups. The distances between the Cu atom and the N atoms of cyclam are 2.018(3) and 2.016(3) Å, while the Cu-$N_{cyanide}$ bond length is 2.578(3) Å (with Cu1 as representative), clearly showing the markedly axially distorted octahedron surrounding of the Cu(II) ion. The angles of C≡N-Cu is 145.7(3) and 150.5(3)°, respectively, demonstrating that these three atoms are somewhat bent from a linear configuration. The intramolecular Fe^{III}-Cu^{II} separation through bridging cyanide is about 5.4 Å, obvious shorter than the shortest intermolecular metal-metal distance with the value 7.8 Å.



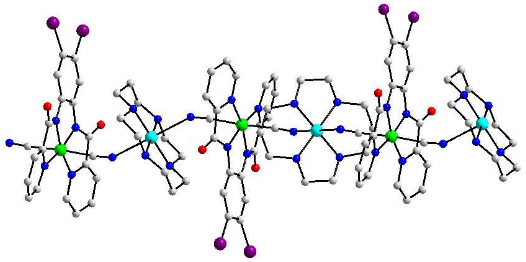


Figure 5. The asymmetry unit and one-dimensional cationic structure of complex **5**. All the hydrogen atoms, the free ClO_4^- and solvent molecules have been omitted for clarity.

Table 3. The selected bond lengths and angles for complexes **3-5**.

	3	4		5
Mn1-N1	2.362(5)	2.340(3)	Cu1-N1	2.578(3)
Mn1-N2#2	2.347(5)	2.301(3)	Cu1-N7#1	2.018(3)
Mn1-N7	1.993(5)	2.019(3)	Cu1-N7	2.018(3)
Mn1-N8	1.995(4)	2.020(3)	Cu1-N8	2.016(3)
Mn1-O1	1.879(4)	1.890(2)	Cu1-N8#1	2.016(3)
Mn1-O2	1.886(4)	1.881(2)	Cu1-N1#1	2.578(3)
Fe1-C1	1.984(6)	1.980(3)	Fe1-C1	1.985(4)
Fe1-C2	1.979(6)	1.982(3)	Fe1-C2	1.982(4)
Fe1-N3	1.895(4)	1.893(3)	Fe1-N3	1.894(3)
Fe1-N4	1.902(4)	2.008(3)	Fe1-N4	1.884(3)
Fe1-N5	2.023(4)	1.889(3)	Fe1-N5	2.007(3)
Fe1-N6	2.013(4)	2.014(3)	Fe1-N6	2.005(3)
C1-N1-Mn1	154.6(4)	150.1(3)	C1-N1-Cu1	145.7(3)
C2-N2-Mn1#1	151.6(4)	146.8(3)	C2-N2-Cu2	150.5(3)

Symmetry transformations used to generate equivalent atoms: **3**: #1 x-1, y, z ; #2 x+1, y, z ; **4**: #1 x+1, y, z ; #2 x-1, y, z ; **5** : #1 -x+1, -y, -z

Magnetic properties of complexes 2-5. The temperature dependence of magnetic susceptibilities for these four complexes was measured in the range of 2-300 K under an external magnetic field of 2000 Oe. The temperature dependence of the $\chi_M T$ for complex **2** is illustrated in Figure 6. The $\chi_M T$ value at room temperature is 0.79 emu K mol^{-1}, slightly higher than the only value of 0.75 emu K mol^{-1} for two uncoupled low spin Fe(III) (S = 1/2) based on g = 2.00. With the temperature decreasing, the $\chi_M T$ value remains almost constant from 300 to about 50 K. After this, the $\chi_M T$ value starts to decrease rapidly and reaches the value of 0.53 emu K mol^{-1}. The magnetic susceptibility conforms well to Curie-Weiss law in the range of 2-300 K and give the negative Weiss constant θ = -1.70 K and Curie constant C = 0.80 emu K mol^{-1}. These data, in combination with the changing tendency of $\chi_M T$-T, lead to the conclusion that the magnetic coupling between the neighbouring Fe(III) ions bridged by cyanide group is antiferromagnetic.

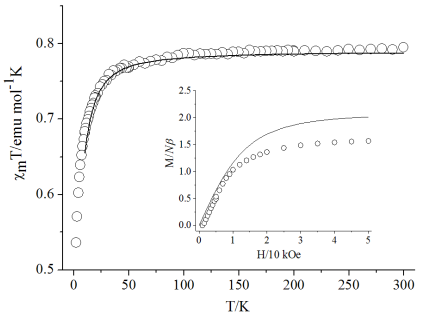


Figure 6. Temperature dependence of $\chi_M T$ of complex **2** (the solid line represents the best fit based on the parameters discussed in the text). Inset: Field dependence of magnetization at 2 K (the line is the Brillouin curve for S = 1/2 +1/2 with g = 2.0).

The alternating chain model based on the following spin Hamiltonian can be used for evaluating the intra-chain coupling:[36]

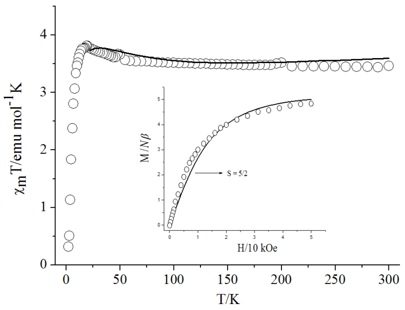
$$\hat{H} = -2J\sum_i (S_i^z S_{i+1}^z + S_i^x S_{i+1}^x + S_i^y S_{i+1}^y)$$

$$\chi_M = \frac{Ng^2\beta^2}{kT}\left[\frac{0.25+0.1495x+0.30094x^2}{1.0+1.9862x+0.66854x^2+6.0626x^3}\right]$$

$$x = \frac{|J|}{kT}$$

The experimental $\chi_M T$ value between 10-300 K were used for fitting, giving the best-fit parameters J = -1.98(2) cm^{-1}, g = 2.02, R = 1.79×10^{-5}. These results further confirm the antiferromagnetic coupling between the cyanide-bridged Fe(III) ions, which can also be supported by the isothermal magnetization measurements at 2 K, as shown in inset of Figure 6. The calculated curve lies above the experimental data, indicating the presence of appreciable antiferromagnetic interaction.

The $\chi_M T$ behaviour for complexes **3** and **4** (Figure 7), whose magnetic susceptibilities varied in a comparatively narrow range, is similar to the reported cyanide-bridged Fe(III)-Mn(III) complexes based on also the similar cyanide precursors.[28d] The room temperature $\chi_M T$ values for these two complexes are 3.46 and 3.48 emu K mol^{-1}, respectively, which are consistent with the spin only value of 3.375 emu K mol^{-1} for uncoupled Mn(III) (S = 2) and low spin Fe(III) (S = 1/2) based on g = 2.00. The $\chi_M T$ values increase with a very low speed and attain their highest peak about 3.8 emu K mol^{-1} with the temperature decreasing to 20 K, and then decrease with a high speed and reach the value of about 0.3 emu K mol^{-1} at 2 K. The decrease in the very low temperature can be attributed to the zero field spitting of the Mn(III) ion and/or the intermolecular antiferromagnetic interaction.



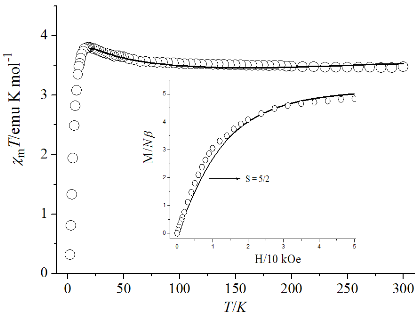
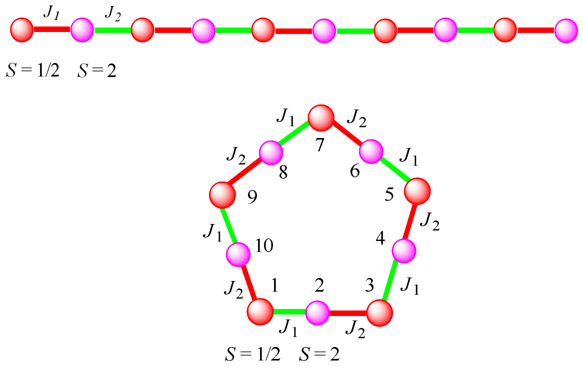


Figure 7. Temperature dependence of $\chi_M T$ of complex **3** and **4** (the solid line represents the best fit based on the parameters discussed in the text). Inset: Field dependence of magnetization at 2 K (the line is the Brillouin curve for S = 5/2 with g = 2.0).

Usually, the nature of the magnetic properties for paramagnetic complexes is governed not only by the magnetic couplings through the bridging groups but also by the spin-orbit coupling effects, zero-field splitting and the intermolecular magnetic interactions. However, it is impossible to simulating the magnetic data by including all the factors above mentioned. Here, the magnetic susceptibilities of these two 1D complexes have been simulated by using the MAGPACK program.[37] Furthermore, considering also that the effects resulted from the intermolecular interaction and the zfs (zero-field splitting) of Mn(III) ion are relatively small and can therefore be safely neglected at relatively high temperature, the data of the experiment $\chi_M T$ value of 20-300 K was used for fitting. According to the method which has been successfully employed to simulate the magnetic susceptibilities of 1D chain compounds,[37,38] these two compounds can be considered as isotropic Heisenberg chain containing alternating spins 1/2 and 2 with two ferromagnetic exchange interactions J_1 and J_2 (Scheme 2), which is base on the fact that the two Mn–N≡C bond angles are not completely equal to each other. In this case, the magnetic susceptibilities of the infinite single chain can be simulated and calculated reasonably satisfactorily based on a closed ring cluster model consisting of five pairs of 1/2-2 spin pairs with two alternating ferromagnetic exchange interactions J_1 and J_2, Scheme 2. The best-fit parameters are J_1 = 0.56(1), J_2 = 0.45(2) cm^{-1} g = 2.01, R = 1.67×10^{-5} for **3** and J_1 = 0.59(3) and J_2 = 0.43(8) cm^{-1} g = 2.03, R = 1.71×10^{-5} for **4**, respectively, demonstrating the ferromagnetic coupling between the cyanide-bridged Fe(III)-Mn(III) in these two complexes. The results are all comparable to those found in other 1D cyanide-bridged Fe(III)-Mn(III) complexes.[28d]



Scheme 2.

The inset of Figure 7 shows the field-dependent magnetization measured up to 50 kOe at 2 K for these two complexes. The magnetization increases rapidly up to 15 kOe, and from then the curve becomes relatively even and attains their maximum value at about 4.90 $N\beta$, which is very close to the saturated value of 5.0 $N\beta$. These data can further confirm the ferromagnetic coupling nature between the Fe(III) and Mn(III) ions in complexes **3** and **4**.

Figure 8 shows the temperature dependence of the magnetic susceptibility of complex **5**. The value at room temperature, 0.9 emu K mol^{-1}, is slightly larger than the spin-only value of 0.75 emu K mol^{-1} expected for isolated Cu^{II} and low spin Fe^{III} (S =□1/2) centers assuming g =□2.0, which is probably due to the orbital contribution to the magnetic moment of the low-spin Fe^{III}. As the temperature is lowered, $\chi_M T$ steadily decreases to a minimum value of 0.82 emu K mol^{-1} at about 70 K. Such a magnetic behaviour is characteristic of a low-spin octahedral iron(III) system with spin-orbit coupling of the $^2T_{2g}$ ground term. A similar temperature dependence of $\chi_M T$ has been observed for the compound containing only paramagnetic $[Fe(CN)_6]^{3-}$.[39] On further lowering the temperature, $\chi_M T$ increases to reach a maximum of 0.92 emu K mol^{-1}and then decreases sharply to a value of 0.76 emu K mol^{-1} at 2 K. The increase in $\chi_m T$ at low temperature is consistent with weak ferromagnetic coupling between the Fe(III) and Cu(II) spins. The magnetic data of complex **5** was simulated by a 1D ferromagnetic chain model based-on the following Hamiltonian.[40] The data of the experiment $\chi_m T$ value of 10-300 K was used for fitting, giving the best-fit parameters $J = 1.77(5)$ cm^{-1}, g = 1.99, $R = 5.28\times10^{-4}$.

$$\hat{H} = -J\sum_i S_i S_{i+1}$$

$$\chi_M = \frac{Ng^2\beta^2}{4kT}\left[\frac{N}{D}\right]^{\frac{2}{3}}$$

$$N = 1.0 + 5.979916Y + 16.902653Y^2 + 29.376885Y^3 + 29.832959Y^4 + 14.036918Y^5$$

$$D = 1.0 + 2.3979916Y + 7.008678Y^2 + 8.6538644Y^3 + 4.5743114Y^4$$

$$Y = J/2kT$$

To confirm the ferromagnetic character, the *M(H)* data for **5** were collected at 2 K, as depicted in the inset of Figure 8. The Brillouin curve is drawn based on uncoupled Fe(III) and Cu(II) spins. At the low field range, the experimental data reside higher than the calculated plot, demonstrating the operation of overall ferromagnetic interactions. Similar magnetic coupling behaviour have also been found in cyanide-bridged Fe(III)Cu(II) or M(V)Cu(II) (M = Mo, W) bimetallic systems bearing axially elongated Cu(II) coordination spheres.[39,41]

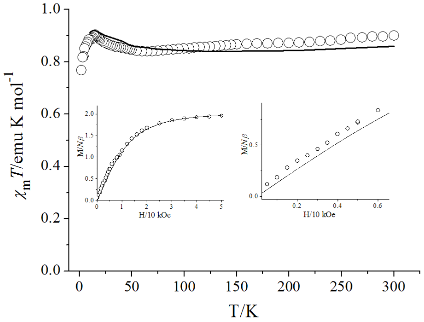


Figure 8. Temperature dependence of $\chi_M T$ of complex **5**. The solid line represents the best fit based on the parameters discussed in the text). Inset: Field dependence of magnetization at 2 K (the dotted line is the Brillouin curve for uncoupled Fe(III) and Mn(II) ions with g = 2.0).

Investigation of the magnetic properties reveals antiferromagnetic coupling between the cyanide-bridged low spin Fe(III) ions in complex **2** and overall ferromagnetic interaction between the low spin Fe(III) and Mn(III)/Cu(II) ions through the bridging cyanide group(s) in complexes **3**-**5**, respectively. As has long been known, the electronic ground state configuration of low spin Fe(III) ion located in an axially elongated octahedron becomes $(d_{xz}, d_{yz})^4(d_{xy})^1$.[34] Therefore, the antiferromagnetic coupling behaviour in complex **1** can be understandable considering that the $(d_{xy})^1$ orbital overlap of the low spin Fe(III) ions. Similar to the Prussian blue family in which the M-C≡N-M' units are perfectly colinear and the metals have regular octahedral coordination geometry, both ferromagnetic exchange (e_g(Mn)-t_{2g}(Fe)) paths (t_{2g}(Mn)-t_{2g}(Fe)) and antiferromagnetic coupling exist simultaneously between Fe(III) and Mn(III) magnetic centers in the system of Fe^{III}-Mn^{III} (low-spin Fe(III) (d^5, t_{2g}^5) and high-spin Mn(III) (d^4, $t_{2g}^3e_g^1$)) due to the strict orthogonality and the overlap of the magnetic orbitals(Figure S2, ESI). However, previous experimental results reveal that the Mn-N$_{ax}$≡C$_{ax}$ angles, as well as the Mn-N$_{ax}$ bond lengths, the torsion angles of C$_{eq}$-Fe-Mn-N(O)$_{eq}$ equivalent to the rotation of the x and z axes for Mn(III) relative to the xz plane and the relative positioning of the magnetic orbital (dπ) in the cyanide precursor, play an important role for tuning the coupling nature in cyanide-bridged Fe(III)-Mn(III) system (Table S1, ESI).[28c, 42] The Mn-N≡C bond angle usually deviates significantly from the strict linear arrangement and frequently forms a bending Mn-N≡C-Fe linkage, which can reduce the overlap between t_{2g}(Fe) and t_{2g}(Mn) orbitals and therefore favouring of the ferromagnetic interaction between Fe(III)-Mn(III) through the cyanide bridge. A recent study[28c] revealed that compounds with C≡N–Mn bond angles below 162° most probably exhibit ferromagnetic interaction with few exceptions, and above 162° both ferromagnetic and antiferromagnetic properties are possible (Table S1, ESI), which is further affirmed by the present complexes with the Mn-N≡C bond angle in the range of 146.8(3)-156.6(4)°.

The copper(II) ion is a Jahn-Teller-active metal ion with the electronic configuration $t_{2g}^6e_g^3$ and tends to afford short, strong equatorial bonds and long, weak axial bonds to the terminal N atoms of the bridging cyanide ligands in cyanide-bridged system. Therefore, the weakly ferromagnetic coupling observed in almost all the reported cyanide-bridged low spin Fe(III)($t_{2g}^5e_g^0$)-Cu(II)($t_{2g}^6e_g^3$) examples can be easily interpreted by the orthogonality of the t_{2g} magnetic orbitals of Fe(III) ion with the e_g one of Cu(II) ion, which have been confirmed by detailed theoretical calculation.[43,44] As can be found in complex **5**, the Cu(II) ion was involved also in a markedly elongated octahedron. The long Cu-N$_{ax}$ lengths cause the overlap between Fe dπ and Cu $d_{x^2-y^2}$ magnetic orbitals to be minimal, therefore further favouring the ferromagnetic communication between the cyanide-bridged Fe(III)-Cu(II).

Conclusion

In summary, a new series of heterobimetallic cyanide-bridged one-dimensional complexes, including the first example of the alternating low spin iron(III) chain, the neutral Fe(III)-Mn(III) chain and the cationic Fe(III)-Cu(II) chain, have been synthesized by using new *trans*-dicyanideioron(III)-containing building block and several paramagnetic Fe(III)/Mn(III)/Cu(II) compounds as assemble segments. Investigation of their magnetic properties reveals an antiferromagnetic interaction between the low spin Fe(III) ions and the ferromagnetic interaction between the low spin Fe(III) ions and Mn(III)/Cu(II) ions bridged by cyanide group. The present work gives further information that such types of the cyanidemetalates are good candidates for the design and synthesis of 1D magnetic complexes. Synthesis and magnetic investigation over other series of cyanide-bridged 1D complexes with interesting magnetic properties, especially as single chain magnets, using appropriate spin carriers as building block are under way.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Crystallographic data in CIF format. The magnetic property of compound **1**. The orbital picture of different magnetic exchange situations with bent Fe-C≡N-Mn linkages. Table with the magneto-structural data for the reported single cyanide-briged low-spin Fe(III)-Mn(III) complexes. See DOI: 10.1039/b000000x/

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