K[Fe(5-Clsalen)(CN)$_2$] as a new building block for heterobimetallic 1-D cyanide-bridged Fe^{III}–Mn^{II} complexes: synthesis, crystal structures, and magnetic properties

Daopeng Zhang [a] , Zengdian Zhao [a] , Ping Wang [a] & Xia Chen [a]

[a] College of Chemical Engineering, Shandong University of Technology , Zibo 255049 , P. R. China
Accepted author version posted online: 01 Jun 2012.Published online: 14 Jun 2012.

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

K[Fe(5-Clsalen)(CN)₂] as a new building block for heterobimetallic 1-D cyanide-bridged Fe^III^–Mn^II^ complexes: synthesis, crystal structures, and magnetic properties

DAOPENG ZHANG*, ZENGDIAN ZHAO, PING WANG and XIA CHEN

College of Chemical Engineering,
Shandong University of Technology, Zibo 255049, P. R. China

With a new *trans*-dicyanideiron(III) precursor $K[Fe(5\text{-Clsalen})(CN)_2] \cdot CH_3OH$ (**1**) (5-ClsalenH$_2$ = N,N′-bis(5-Clsalicyl)ethylenediamine) as building block and two Mn(II) compounds containing 15-membered macrocycle rings as assembling segments, two new 1-D, cyanide-bridged heterometallic Fe^III^–Mn^II^ complexes, $\{[Fe(5\text{-Clsalen})(CN)_2][Mn(L^1)]\}ClO_4 \cdot H_2O$ (**2**), and $\{[Fe(5\text{-Clsalen})(CN)_2][Mn(L^2)]\}ClO_4$ (**3**), have been successfully synthesized and characterized by elemental analysis, IR spectroscopy, and X-ray structure determination. Single X-ray diffraction analysis reveals 1-D, cyanide-bridged cationic polymeric single chains for **2** and **3** consisting of alternating units of $[Mn(L)]^{2+}$ (L = L^1 and L^2) and $[Fe(5\text{-Clsalen})(CN)_2]^-$ with free ClO_4^-. Magnetic properties of these two heterometallic cyanide-bridged Fe^III^–Mn^II^ complexes reveal the overall antiferromagnetic interaction between neighboring Fe(III) and Mn(II) through cyanide bridges. A best-fit to the magnetic susceptibilities of **2** and **3** based on the 1-D alternating chain model leads to magnetic coupling constants $J_1 = -2.95(1)$, $J_2 = -0.81(5)\,cm^{-1}$ for **2** and $J_1 = -2.37(2)$, $J_2 = -0.35(1)\,cm^{-1}$ for **3**, respectively.

Keywords: Cyanide-bridged; Heterobimetallic 1-D chain; Crystal structure; Magnetic property

1. Introduction

Cyanide groups show some unique characteristics in preparing heterometallic molecular magnetic materials with various structures [1–5], such as spin crossover (SCO), photomagnetic materials, single-molecule magnets (SMMs) and single-chain magnets (SCMs) [6–16]. Thus far, a number of polycyanideiron(III) building blocks, including $[Fe(L)(CN)_5]^{2-}$ (L = 1-methylimidazole), $[Fe(L)(CN)_4]^-$ (L = bipy, phen, bpym), *fac*-$[Fe(L)(CN)_3]^-$ (L = Tp, Tp*, pzTp, tach), *mer*-$[Fe(L)(CN)_3]^-$ (L = bpca, pzcq, mpzcq, qcq, pcq) [17–23], and our recent work based on $[Fe(L)(CN)_2]^-$ (L = bpb derivatives bpb^{2-} = 1,2-bis(pyridine-2-carboxamido)benzenate) [24], have been synthesized and employed in assembling low-dimensional, cyanide-bridged molecular magnetic materials. However, the blocking ligand in polycyanideiron(III) building blocks $[Fe(L)(CN)_m]^{n-}$ has been restricted to nitrogen-containing ligands such as neutral

---

*Corresponding author. Email: dpzhang73@126.com
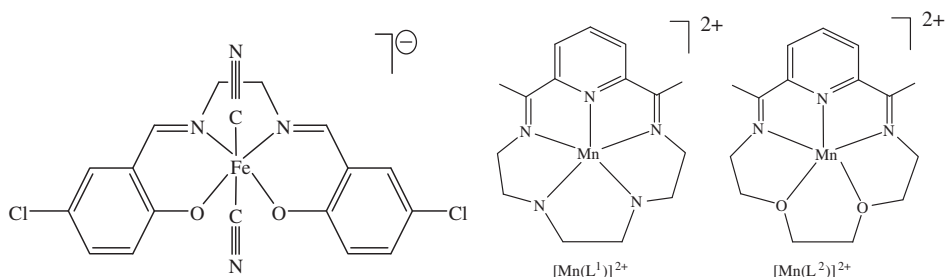
Scheme 1. The reactant precursors used to synthesize complexes **2** and **3**.

monodentate imidazole-type ligands, bidentate pyridine-type ligands, ionic tridentate pyrazole-, pyridineimide-, pyridineamide-type ligands, and ionic tetradentate pyridineamide-type ligands, except the work based on $K[Fe(Salen)(CN)_2]$ reported by our group [25b].

Our recent research showed that the position and size of the substituent on the Schiff-base ligand has obvious influence on the structure and magnetic property of the formed cyanide-bridged heterometallic complexes [26]. To compare the structure and magnetic properties of the cyanide-bridged complexes assembled from different cyanide precursors, a new *trans*-dicyanideiron(III) precursor based on the substituted salen, $[Fe(5\text{-}Clsalen)(CN)_2]^-$ (scheme 1), which has been structurally characterized here, has been employed to prepare new cyanide-bridged bimetallic systems. Two cyanide-bridged single-chain Fe(III)–Mn(II) heterobimetallic complexes, {[Fe(5-Clsalen)(CN)_2][Mn(L^1)]}ClO_4 · H_2O (**2**), and {[Fe(5-Clsalen)(CN)_2][Mn(L^2)]}ClO_4 (**3**), including their synthesis, crystal structures, and magnetic properties, will be described in this article. Cyanide-bridged Fe^{III}–Mn^{II} complexes with perfect single-chain structure remain very rare [24d, 25b] despite reports on several examples with double zigzag chain structures.

2. Experimental

2.1. *Physical measurements*

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementar Vario El. Infrared spectroscopy on KBr pellets was performed on a Magna-IR 750 spectrophotometer from 4000 to $400 \, cm^{-1}$. Variable-temperature magnetic susceptibility and field-dependent 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).

2.2. *General procedures and materials*

All chemicals and solvents used for the synthesis were of reagent grade without purification. The synthesis of 5-ClsalenH_2 was carried out by the condensation of 5-chloro-2-hydroxy-benzaldehyde and 1,2-diaminoethane with a ratio of 2 : 1 in ethanol.

K[Fe(5-Clsalen)(CN)$_2$] was prepared using a modified method reported for Na[Fesalen)(CN)$_2$] [27]. [Mn(L^1)(H$_2$O)Cl]ClO$_4$ and [Mn(L^2)(H$_2$O)Cl]ClO$_4$ were synthesized according to the reports [25].

2.3. *Preparation of K[Fe(5-Clsalen)(CN)₂]·CH₃OH (1)*

To a solution of 5-ClH$_2$salen (337 mg, 1.0 mmol) in methanol (50 mL), FeCl$_3$·6H$_2$O (166 mg, 1.0 mmol) was slowly added. The mixture was refluxed for 3 h before KCN (130 mg, 2 mmol) was added to the formed solution, and the suspension was stirred at 60°C until the color of the mixture changed from red-brown to dark green; then the solution was filtered to remove insoluble materials when hot. The filtrate was concentrated to 10 mL under reduced pressure and excess ether was added. Then, the precipitated dark-green solid was collected by filtration, washed with ether, and dried under vacuum. Yield: 333 mg, 65%. Anal. Calcd for C$_{19}$H$_{14}$Cl$_2$FeKN$_4$O$_3$ (%): C, 44.55; H, 2.76; N, 10.94. Found (%): C, 44.37; H, 2.81; N, 10.79. Main IR bands (KBr, cm^{-1}): 2140s(νC≡N), 1624 vs(νC=N).

2.4. *Synthesis of {[Fe(5-Clsalen)(CN)₂][Mn(L¹)]}ClO₄·H₂O (2) and {[Fe(5-Clsalen)(CN)₂][Mn(L²)]}ClO₄ (3)*

K[Fe(5-Clsalen)(CN)$_2$]·CH$_3$OH (103 mg, 0.20 mmol) dissolved in methanol and water 10 mL (4 : 1, v : v) was added to a methanol solution (10 mL) of [Mn(L^1)(H$_2$O)Cl]ClO$_4$ (48.1 mg, 0.1 mmol) or [Mn(L^2)(H$_2$O)Cl]ClO$_4$ (48.3 mg, 0.1 mmol). The mixture was stirred for 1 min at room temperature and filtered to remove any insoluble material, and then the filtrate was allowed to evaporate slowly without disturbance for 1 week. Dark-brown, needle-like crystals suitable for X-ray diffraction were collected by filtration, washed with cool methanol, and dried in air.

Complex **2**: Yield: 48.9 mg, 55%. Anal. Calcd for C$_{33}$H$_{37}$Cl$_3$FeMnN$_9$O$_7$ (%): C, 44.59; H, 4.20; N, 14.18. Found (%): C, 44.68; H, 4.33; N, 14.08. Main IR bands (KBr, cm^{-1}): 2125 (s, νC≡N), 1626 (vs, νC=N), 1099 (vs, νCl–O).

Complex **3**: Yield: 53.3 mg, 61.1%. Anal. Calcd for C$_{33}$H$_{33}$Cl$_3$FeMnN$_7$O$_8$ (%): C, 45.41; H, 3.81; N, 11.23. Found (%): C, 45.47; H, 3.75; N, 11.41. Main IR bands (KBr, cm^{-1}): 2124 (s, νC≡N), 1621 (vs, νC=N), 1097 (vs, νCl–O).

2.5. *X-ray data collection and structure refinement*

Single crystals of **1**–**3** with suitable dimensions for X-ray diffraction analyses were mounted on glass rods and data were collected on a Bruker SMART CCD diffractometer with a Mo-Kα sealed tube ($\lambda = 0.71073$ Å) at 293 K using a ω scan mode. All structures were solved by direct methods and refined by full matrix least-squares (SHELXTL-97) on F^2. All nonhydrogen atoms, except the disordered ones, were refined with anisotropic displacement coefficients. Oxygen atoms of ClO$_4^-$ and solvent water in **2** are disordered, for which the partially occupied atoms were refined isotropically with an individual occupancy of 50%. All hydrogen atoms were added geometrically, refined by a riding model and assigned isotropic displacement

Table 1. Crystallographic data for **1–3**.

	1	**2**	**3**
Empirical formula	$C_{19}H_{14}Cl_2FeKN_4O_3$	$C_{33}H_{37}Cl_3FeMnN_9O_7$	$C_{33}H_{33}Cl_3FeMnN_7O_8$
Formula weight	512.19	888.86	872.80
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)	P2(1)/n	P2(1)/n
Unit cell dimensions (Å, °)			
a	11.28680(10)	14.856(3)	14.908(9)
b	7.73120(10)	18.083(4)	18.264(11)
c	12.2914(2)	14.927(3)	14.955(9)
β	102.0460(10)	91.073(4)	90.30(2)
Volume ($Å^3$), Z	1048.94(2), 2	4009.4(15), 4	4072(4), 4
Completeness	99.6%	97.5%	97.6%
$F(000)$	518	1824	1784
θ range for data collection (°)	1.84–25.00	1.95–25.01	2.23–24.50
Goodness-of-fit on F^2	1.004	1.005	1.012
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0246$, $wR_2 = 0.0713$	$R_1 = 0.0806$, $wR_2 = 0.2538$	$R_1 = 0.0740$, $wR_2 = 0.1957$

coefficients $U(H) = 1.2U(C)$ or $1.5U(C)$, except some hydrogen atoms of solvent. These were refined isotropically with fixed U values and the DFIX command was used to rationalize the bond parameter. Details of the crystal parameters, data collection, and refinement are summarized in table 1.

3. Results and discussion

3.1. *Synthesis and general characterization*

To prepare low-dimensional cyanide-bridged complexes, the factors such as the number and position of cyanides, charge of cyanide-containing building blocks, and steric effects of reactants must be taken into consideration. Introducing ancillary ligand into the cyanide-containing polycyanideiron(III) precursor, especially bulky ones, has been demonstrated as an efficient method to lower the dimensionality of target complexes due to steric effects [24, 25b]. Under this consideration, a new type of cyanideiron(III) building block $[Fe(5\text{-}Clsalen)(CN)_2]^-$ containing two *trans* cyanides and a large equatorial in-plane tetradentate Schiff-base ligand has been designed, prepared, and employed to assemble cyanide-bridged complexes.

Ancillary ligands attached to the assembling cations can also influence the structure and the magnetic property of the resulting complexes. As a result, two Mn(II) compounds containing 15-membered macrocycles, shown in scheme 1, L^1 and L^2, were chosen to act as assembling cation. Both macrocyclic ligands in $[Mn(L^1)(H_2O)Cl]ClO_4$ or $[Mn(L^2)(H_2O)Cl]ClO_4$ coordinate to the equatorial plane of Mn^{II}, forming two seven-coordinate Mn(II) compounds with two *trans* replaceable sites being occupied by H_2O and Cl^- in the present case. Assembling with $K[Fe(5\text{-}Clsalen)(CN)_2]$ using these seven-coordinate Mn(II) compounds is expected to produce complexes with low dimensionality [28, 29].

Table 2. Selected bond lengths and angles for **1**.

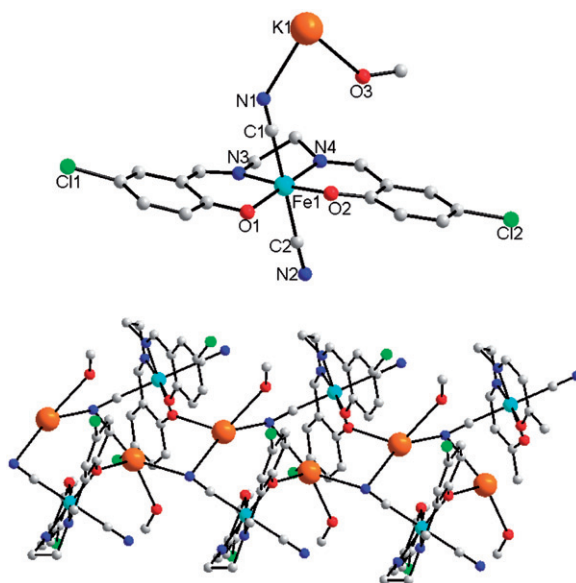|			
Fe1–C1	1.964(3)	Fe1–O2	1.9157(15)
Fe1–C2	1.985(3)	Fe1–N3	1.9127(19)
Fe1–O1	1.9093(17)	Fe1–N4	1.905(2)
Fe1–C1–N1	176.6(2)	Fe1–C2–N2	178.7(3)

Figure 1. The crystal structure of **1** (top) and its double chain structure formed by K–O and K–N interactions (bottom). All hydrogens and methanol have been omitted for clarity.

The new cyanide-containing precursor and the two cyanide-bridged heterometallic Fe^{III}–Mn^{II} complexes were characterized by IR spectroscopy. In **1**, the broad absorption at $2140\,cm^{-1}$ was assigned to the terminal cyanide, while one sharp peak due to cyanide-stretch for **2** and **3** were observed at $2120–2130\,cm^{-1}$, indicating bridging cyanides. In addition, a strong broad peak observed at about $1100\,cm^{-1}$ in the IR spectra of **2** and **3** suggests the presence of ClO_4^-.

3.2. Crystal structures of 1–3

Selected bond lengths and angles for **1** are given in table 2, and its crystal structure and the double chain structure formed by intermolecular K–O and K–N interactions are shown in figure 1. Compound **1** possessing a low-spin central Fe(III) contains octahedral mono-anion [Fe(5-Clsalen)(CN)$_2$]$^-$. Fe(III) is six-coordinate by an equatorial N$_2$O$_2$ unit from the tetradentate Schiff-base ligand and two axial nitrogen atoms from two cyanides. The Fe–C bond lengths are 1.964(3) and 1.985(3) Å, respectively, slightly longer than the Fe–O and Fe–N bond lengths, indicating slightly distorted

Table 3. Selected bond lengths and angles for **2** and **3**.

	2	**3**		**2**	**3**
Mn1–N1	2.281(6)	2.282(9)	Fe1–N3	1.895(6)	1.922(8)
Mn1–N2	2.283(6)	2.260(9)	Fe1–N4	1.908(6)	1.928(8)
Mn1–N5	2.234(7)	2.259(9)	Fe1–O1	1.909(5)	1.917(6)
Mn1–N6	2.316(8)	2.322(10)	Fe1–O2	1.880(5)	1.904(7)
Mn1–N7	2.340(12)	2.312(11)	N1–Mn1–N2	173.8(2)	173.9(3)
Mn1–N8/O8	2.299(11)	2.317(13)	C1–N1–Mn1	168.7(6)	161.8(9)
Mn1–N9/O7	2.263(8)	2.416(13)	C2#1–N2–Mn1	163.0(7)	167.6(8)
Fe1–C1	1.987(7)	1.956(10)	N1–C1–Fe1	176.8(7)	176.5(10)
Fe1–C2	1.976(7)	1.967(11)	N2#2–C2–Fe1	179.2(8)	177.7(9)

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

octahedral coordination sphere of Fe(III). The Fe1–C1≡N1 and Fe1–C2≡N2 are linear with angles very close to 180°.

Selected bond lengths and angles for **2** and **3** are given in table 3. The asymmetric cationic units and 1-D cationic chain structures of **2** and **3** are shown in figures 2 and 3, respectively; representative cell-packing diagram for these two complexes are depicted in figure 4. These two complexes possess similar 1-D cationic single chain structures comprised of repeating [–NC–Fe(5-Clsalen)–CN–Mn(L)–] units with the positive charge balanced by ClO_4^- anions. Each $[Fe(5\text{-}ClSalen)(CN)_2]^-$ is bidentate through its two *trans* cyanides, linking Mn(II) of two independent macrocyclic manganese units. Similar to **1**, the coordination sphere of the Fe(III) is a distorted octahedron. The bond angles of Fe–C≡N in these two complexes are very close to each other with the value of *ca* 177°, also close to those in **1**, indicating clearly that the three atoms are in a good linear configuration.

The Mn(II) ions in **2** and **3** are seven-coordinate, forming a slightly distorted pentagonal–bipyramidal coordination geometry, in which the five equatorial positions are occupied by N_5 or N_3O_2 coming from the macrocyclic ligand and two axial positions coordinated by two nitrogen atoms of cyanide. The distances between Mn and equatorial N or O (table 2) are in agreement with those found in precursors $[Mn(L)(H_2O)Cl]ClO_4$ and $[Mn(L^1)(H_2O)_2]Cl_2$ [30]. The Mn–$N_{cyanide}$ bond lengths in these complexes are 2.281(6), 2.283(6) and 2.282(9), 2.260(9) Å, respectively, consistent with Mn–$N_{equatorial}$ bond lengths. As tabulated in table 2, the N1–Mn1–N2 bond angle is 174°, indicating a linear configuration. However, the Mn–N≡C bond angles are somewhat bent with the values of 168.7(6), 163.0(7) and 161.8(9), 167.6(8)° in **2** and **3**, respectively, suggesting slight deviation from linear. The intramolecular Fe^{III}–Mn^{II} separation through bridging cyanide(s) in **2** and **3** are 5.385 and 5.299 Å, respectively, while the shortest inter-chain, metal–metal distances, 8.348 and 8.815 Å, are obviously longer than this value.

3.3. *Magnetic properties of 2 and 3*

The magnetic susceptibilities of **2** and **3** were measured from 2 to 300 K under an applied magnetic field of 2000 Oe. As shown in figure 5, the changing tendency of $\chi_M T$ for these complexes is very similar. The $\chi_M T$ value at room temperature is 4.54 and 4.63 emu K mol^{-1} for **2** and **3**, respectively, slightly lower than the spin only value of
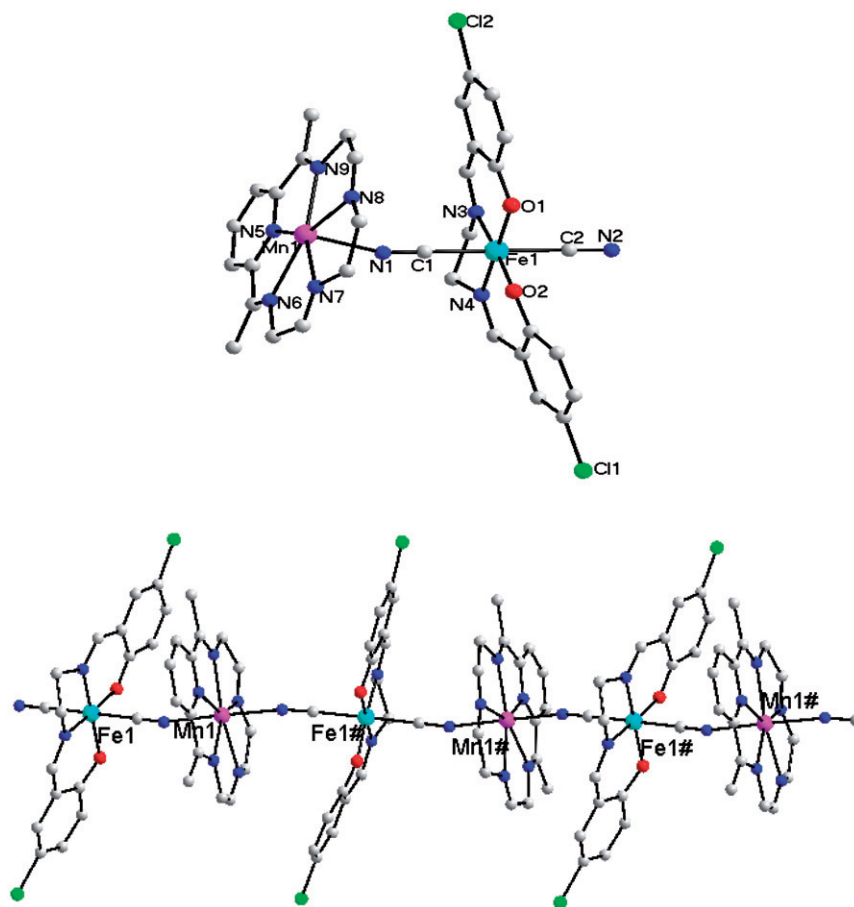
Figure 2. The asymmetric cation and one-dimensional cation chain of **2**. All hydrogen atoms, free ClO_4^-, and solvent water molecule have been omitted for clarity. The symmetry code used to generate Fe1# and Mn1#: $x + 1/2$, $-y + 3/2$, $z - 1/2$.

4.75 emu K mol^{-1} for uncoupled Mn(II) ($S = 5/2$) and low-spin Fe(III) ($S = 1/2$) based on $g = 2.00$. Upon lowering the temperature, the $\chi_M T$ decreases slowly until about 75 K, then decreases rapidly and reaches a value of 3.15 emu K mol^{-1} for **2** at 7 K and 3.84 emu K mol^{-1} for **3** at 10 K, and then the $\chi_M T$ begins to increase sharply from this point, attaining 3.97 emu K mol^{-1} for **2** and 4.79 emu K mol^{-1} for **3** with a temperature decrease to 2 K. The magnetic susceptibilities for these two complexes conform well to the Curie–Weiss law in the range 2–300 K and give the negative Weiss constant $\theta = -1.89$ K and Curie constant $C = 4.55$ emu K mol^{-1} for **2** and $\theta = -2.73$ K, $C = 4.68$ emu K mol^{-1} for **3**, respectively. These data, together with the changing tendency of $\chi_M T$–T considered, result in the conclusion that the magnetic coupling between cyanide-bridged Fe(III) and Mn(II) in **2** and **3** is antiferromagnetic.

To analyze the magnetic data of these two 1-D heterometallic Fe^{III}–Mn^{II} single chains, an approach similar to that previously used for heterometallic 1-D and quasi-2-D complexes was employed [31, 32]. According to the crystal data, the Fe(III)–CN–Mn(II) linkages in these two complexes are unequal. Therefore, the 1-D single chain can
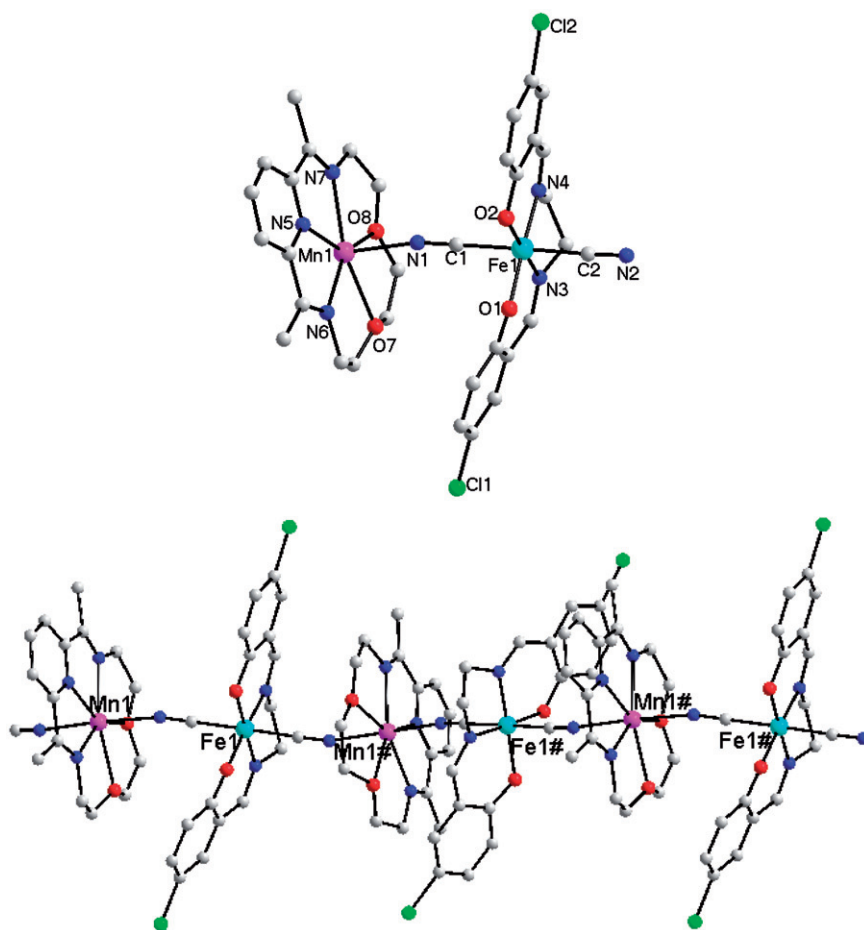
Figure 3. The asymmetric cation and 1-D chain structure of **3**. All hydrogen atoms and free ClO_4^- have been omitted for clarity. The symmetry code used to generate Fe1# and Mn1#: $x + 1/2$, $-y + 3/2$, $z - 1/2$.

be treated as alternating uniform Fe^{III}–Mn^{II} dimers with different intradimeric and intrachain (also interdimer) exchange constants (J_1 *vs.* J_2) (scheme 2).

By using this model, susceptibilities from 2 to 300 K for **2** and **3** were simulated, giving the best-fit parameters $J_1 = -2.95(1)$, $J_2 = -0.81(5)\,cm^{-1}$, $zJ' = -0.14(2)\,cm^{-1}$, $g = 2.00(4)$, $R = \sum(\chi_{Obsd}T - \chi_{Calcd}T)^2/\sum(\chi_{Obsd}T)^2 = 1.65 \times 10^{-5}$ for **2** and $J_1 = -2.37(2)$, $J_2 = -0.35(1)\,cm^{-1}$, $zJ' = -0.11(8)\,cm^{-1}$, $g = 1.99(6)$, $R = 2.07 \times 10^{-5}$ for **3**. These results are comparable to those of cyanide-bridged Fe^{III}–Mn^{II} 1-D complexes assembled based on *trans*-dicyanideiron(III) precursors [24d, 25b].

Both of the cyanide-bridged, 1-D Fe^{III}–Mn^{II} complexes show overall antiferromagnetic coupling between cyanide-bridged Fe(III) and Mn(II). Usually, the presence of a net overlap of the magnetic orbitals through the σ–π (t_{2g}–e_g) ferromagnetic orthogonal coupling is weaker than the antiferromagnetic term through the $\pi(t_{2g}$–$t_{2g})$ pathways ($t_{2g}^3 e_g^2$ and $t_{2g}^5 e_g^0$ configurations for Mn(II) and Fe(III), respectively) for these compounds. The Mn–C≡N angles in these two complexes, which can directly effect
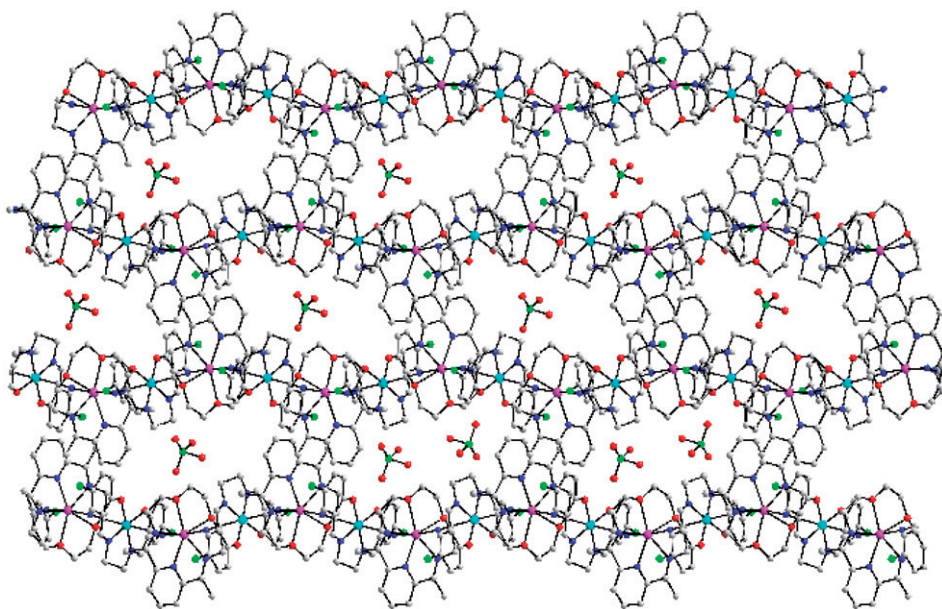
Figure 4. The representative cell packing diagram for **2** and **3** along the *a* axis with ClO_4^- filling the space of the one-dimensional chains. All hydrogen atoms have been omitted for clarity.
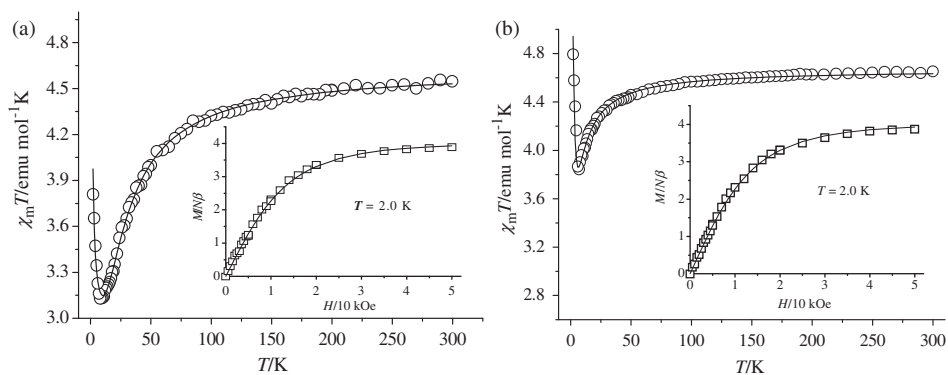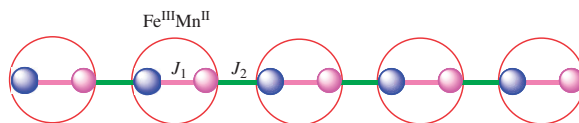
Figure 5. Temperature dependence of $\chi_M T$ for **2** (a) and **3** (b) (the solid line represents the best fit based on the parameters discussed in the text). Inset: Field dependence of magnetization at 2 K (the dotted line is the Brillouin curve for coupled Fe(III) and Mn(II) ions with $g = 2.0$).

Scheme 2. The model used to analyze the magnetic data of complexes **2** and **3**.

the overlap of the magnetic orbitals, are similar to those found in the cyanide-bridged Fe(III)–Mn(II) complexes reported recently, resulting in a magnetic coupling similar to that reported for cyanide-bridged Fe^{III}–Mn^{II} complexes. This work further confirms that most cyanide-bridged Fe^{III}–Mn^{II} complexes exhibit antiferromagnetic interaction.

The field-dependent magnetizations measured up to 50 kOe at 2 K for **2** and **3** are shown in the inset of figure 5. The two curves are similar with magnetization increasing relatively rapidly with increasing field until 15 kOe, then smoothly to 3.9 $N\beta$ at 50 kOe. This is very close to the saturated value of 4.0 $N\beta$, but obviously lower than the value of uncoupled Mn(II) and low-spin Fe(III) based on $g = 2.0$, further confirming the overall antiferromagnetic coupling interaction between Fe(III) and Mn(II) bridged by cyanide.

4. Conclusion

A new *trans*-dicyanideiron(III) precursor K[Fe(5Clsalen)(CN)$_2$] was used as a building block to assemble cyanide-bridged complexes, and two heterobimetallic Fe(III)–Mn(II) complexes with single-chain structures have been synthesized and structurally characterized. Investigation of magnetic properties reveals an overall antiferromagnetic interaction between Fe(III) and Mn(II) bridged by cyanide. The present result indicates that these types of cyanide precursors reported by our group [24, 25b] containing two *trans* cyanides and a large equatorial in-plane ligand are suitable cyanide-containing building blocks with potential for assembling low-dimensional, cyanide-bridged complexes with the desired molecular structures and possible interesting magnetic properties such as SCMs.

Supplementary material

CCDC 856437, 856436 and 856435 contain the supplementary crystallographic data for **1**–**3**. These data can be obtained free of charge *via* http://www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: +44 1223 336 033; or E-mail: deposit@ccdc.cam.ac.uk.

$$\chi_d = \frac{Ng^2\beta^2}{kT} \frac{28 + 10\exp(-6J_1/kT)}{7 + 5\exp(-6J_1/kT)} \tag{1}$$

$$\chi_d = \frac{Ng^2\beta^2}{3kT} S_d(S_d + 1) \tag{2}$$

$$\chi_{chain} = \frac{Ng^2\beta^2}{3kT} \frac{1 + u}{1 - u} \times S_d(S_d + 1) \tag{3}$$

$$\chi_M = \frac{\chi_{chain}}{1 - \chi_{chain}(2zJ'/Ng^2\beta^2)} \tag{4}$$

where $u = \coth(J_2 S_d(S_d + 1)/kT) - kT/J_2 S_d(S_d + 1)$.

Acknowledgments

References

[1] M. Verdaguer, A. Bleuzen, V. Marvaud, J. Vaissermann, M. Seuleiman, C. Desplanches, A. Sciuller, C. Train, R. Garde, G. Gelly, C. Lomenech, I. Rosenman, P. Veillet, C. Cartier, F. Villain. *Coord. Chem. Rev.*, **190–192**, 1023 (1999).

[2] (a) P.V. Bernhardt, F. Bozoglián, B.P. Macpherson, M. Martínez. *Coord. Chem. Rev.*, **249**, 1902 (2005); (b) R. Lescouëzec, L.M. Toma, J. Vaissermann, M. Verdaguer, F.S. Delgado, C. Ruiz-Pérez, F. Lloret, M. Julve. *Coord. Chem. Rev.*, **249**, 2691 (2005).

[3] (a) H. Miyasaka, A. Saitoh, S. Abe. *Coord. Chem. Rev.*, **251**, 2622 (2007); (b) S. Wang, X.H. Ding, J.L. Zuo, X.Z. You, W. Huang. *Coord. Chem. Rev.*, **255**, 1713 (2011).

[4] L. Liu, M. Liu, X.F. Bian, H.S. Wu, M.X. Xu. *J. Coord. Chem.*, **63**, 3907 (2010).

[5] (a) Y.M. Gayfulin, A.I. Smolentsev, Y.V. Mironov. *J. Coord. Chem.*, **64**, 3832 (2011); (b) K.R. Ranjan, A. Singh, A. Banerjee, B. Singh. *J. Coord. Chem.*, **64**, 805 (2011); (c) A. Panja. *J. Coord. Chem.*, **64**, 987 (2011).

[6] V. Niel, A.L. Thompson, M.C. Muñoz, A. Galet, A.E. Goeta, J.A. Real. *Angew. Chem., Int. Ed.*, **42**, 3760 (2003).

[7] G. Agustí, M.C. Muñoz, J.A. Real. *Inorg. Chem.*, **47**, 2552 (2008).

[8] G. Agustí, M.C. Muñoz, A.B. Gaspar, J.A. Real. *Inorg. Chem.*, **49**, 3371 (2009).

[9] O. Sato. *Acc. Chem. Res.*, **36**, 692 (2003).

[10] J. Long, L.M. Chamoreau, C. Mathoniére, V. Marvaud. *Inorg. Chem.*, **48**, 22 (2009).

[11] (a) A. Bleuzen, V. Marvaud, C. Mathoniere, B. Sieklucka, M. Verdaguer. *Inorg. Chem.*, **48**, 3453 (2009), and references therein; (b) D.P. Zhang, L.F. Zhang, Y.T. Chen, H.L. Wang, Z.H. Ni, W. Wernsdorfer, J.Z. Jiang. *Chem. Commun.*, **46**, 3550 (2010).

[12] (a) J.J. Sokol, A.G. Hee, J.R. Long. *J. Am. Chem. Soc.*, **124**, 7656 (2002); (b) C.P. Berlinguette, D. Vaughn, C. Cañada-Vilalta, J.R. Galán-Mascarós, K.R. Dunbar. *Angew. Chem., Int. Ed.*, **42**, 1523 (2003); (c) Z.H. Ni, H.Z. Kou, L.F. Zhang, C. Ge, A.L. Cui, R.J. Wang, Y. Li, O. Sato. *Angew. Chem., Int. Ed.*, **44**, 7742 (2005).

[13] (a) J.H. Yoon, J.H. Lim, H.C. Kim, C.S. Hong. *Inorg. Chem.*, **45**, 9613 (2006); (b) M. Atanasov, P. Comba, Y.D. Lampeka, G. Linti, T. Malcherek, R. Miletich, A.I. Prikhod'ko, H. Pritzkow. *Chem. Eur. J.*, **12**, 737 (2006); (c) M. Atanasov, C. Busche P. Comba, F. El Hallak, B. Martin, G. Rajaraman, J. van Slageren, H. Wadepohl. *Inorg. Chem.*, **47**, 8112 (2008).

[14] H. Miyasaka, M. Julve, M. Yamashita, R. Clérac. *Inorg. Chem.*, **48**, 3420 (2009).

[15] C. Avendano, M.G. Hilfiger, A. Prosvirin, C. Sanders, D. Stepien, K.R. Dunbar. *J. Am. Chem. Soc.*, **132**, 13123 (2010).

[16] W.W. Ni, Z.H. Ni, A.L. Cui, X. Liang, H.Z. Kou. *Inorg. Chem.*, **46**, 22 (2007).

[17] (a) R. Lescouëzec, J. Vaissermann, C. Ruiz-Pérez, F. Lloret, R. Carrasco, M. Julve, M. Verdaguer, Y. Dromzee, D. Gatteschi, W. Wernsdorfer. *Angew. Chem., Int. Ed.*, **42**, 1483 (2003); (b) L.M. Toma, R. Lescouëzec, J. Pasán, C. Ruiz-Pérez, J. Vaissermann, J. Cano, R. Carrasco, W. Wernsdorfer, F. Lloret, M. Julve. *J. Am. Chem. Soc.*, **128**, 4842 (2006).

[18] (a) H.R. Wen, C.F. Wang, Y. Song, S. Gao, J.L. Zuo, X.Z. You. *Inorg. Chem.*, **45**, 8942 (2006); (b) S. Wang, J.L. Zuo, H.C. Zhou, H.J. Choi, Y. Ke, J.R. Long, X.Z. You. *Angew. Chem., Int. Ed.*, **43**, 5940 (2004); (c) S. Wang, J.L. Zuo, S. Gao, Y. Song, H.C. Zhuo, Y.Z. Zhang, X.Z. You. *J. Am. Chem. Soc.*, **126**, 8900 (2004).

[19] D. Li, S. Parkin, G. Wang, G.T. Yee, R. Clérac, W. Wernsdorfer, S.M. Holmes. *J. Am. Chem. Soc.*, **128**, 4214 (2006).

[20] J.Y. Yang, M.P. Shores, J.J. Sokol, J.R. Long. *Inorg. Chem.*, **42**, 1403 (2003).

[21] R. Lescouëzec, J. Vaissermann, L.M. Toma, R. Carrasco, F. Lloret, M. Julve. *Inorg. Chem.*, **43**, 2234 (2004).

[22] (a) Jae II Kim, H.S. Yoo, E.K. Koh, H.C. Kim, C.S. Hong. *Inorg. Chem.*, **46**, 8481 (2007); (b) Jae II Kim, H.Y. Kwak, J.H. Yoon, D.W. Ryu, I.Y. Yoo, N. Yang, B.K. Cho, J.G. Park, H. Lee, C.S. Hong. *Inorg. Chem.*, **48**, 2956 (2009).

[23] Z.H. Ni, H.Z. Kou, L.F. Zhang, W.W. Ni, Y.B. Jiang, A.L. Cui, J. Ribas, O. Sato. *Inorg. Chem.*, **44**, 9631 (2005).

[24] (a) Z.H. Ni, H.Z. Kou, L. Zheng, Y.H. Zhao, L.F. Zhang, R.J. Wang, A.L. Cui, O. Sato. *Inorg. Chem.*, **44**, 4728 (2005); (b) Z.H. Ni, H.Z. Kou, Y.H. Zhao, L. Zheng, R.J. Wang, A.L. Cui, O. Sato. *Inorg. Chem.*, **44**, 2050 (2005); (c) Z.H. Ni, L.F. Zhang, V. Tangoulis, W. Wernsdorfer, A.L. Cui, O. Sato, H.Z. Kou. *Inorg. Chem.*, **46**, 6029 (2007); (d) D.P. Zhang, H.L. Wang, Y.T. Chen, Z.N. Ni, L.J. Tian, J.Z. Jiang. *Inorg. Chem.*, **48**, 5488 (2009).

[25] (a) B. Drahoš, J. Kotek, P. Hermann, I. Lukeš, É. Tóth. *Inorg. Chem.,* **49**, 3224 (2010); (b) D.P. Zhang, H.L. Wang, Y.T. Chen, Z.N. Ni, L.J. Tian, J.Z. Jiang. *Dalton Trans.*, 9418 (2009).

[26] D.P. Zhang, H.L. Wang, Y.T. Chen, Z.H. Ni, L.J. Tian, J.Z. Jiang. *Inorg. Chem.*, **48**, 11215 (2009).

[27] M. Gulotti, L. Casella, A. Pasini, R. Ugo. *J. Chem. Soc., Dalton Trans.*, 345 (1977).

[28] (a) F. Bonadio, M.-C. Senna, J. Ensling, A. Sieber, A. Neels, H. Stoeckli-Evans, S. Decurtins. *Inorg. Chem.*, **44**, 969 (2005); (b) A. Kaur Sra, M. Andruh, O. Kahn, S. Golhen, L. Ouahab, J.V. Yakhmi. *Angew. Chem. Int. Ed.*, **38**, 2606 (1999); (c) G. Rombaut, S. Golhen, L. Ouahab, C. Mathonière, O. Kahn. *J. Chem. Soc., Dalton Trans.*, 3609 (2000).

[29] (a) C. Paraschiv, M. Andruh, Y. Journaux, Z. Žak, N. Kyritsakas, L. Ricard. *J. Mater. Chem.*, **16**, 2660 (2006); (b) R. Pradhan, C. Desplanches, P. Guionneau, J.P. Sutter. *Inorg. Chem.*, **42**, 6607 (2003).

[30] O. Jiménez-Sandoval, D. Ramírez-Rosales, M.J. Rosales-Hoz, M.E. Sosa-Torres, R. Zamorano-Ullo. *J. Chem. Soc., Dalton Trans.*, 1551 (1998).

[31] S.G. Kang, K. Ryu, S.K. Jung, J. Kim. *Inorg. Chim. Acta*, **293**, 140 (1999).

[32] (a) B. Chiari, A. Cinti, O. Piovesana, P.F. Zanazzi. *Inorg. Chem.*, **34**, 2652 (1995); (b) M.C. Burla, B. Chiari, A. Cinti, O. Piovesana. *Mol. Cryst. Liq. Cryst.*, **273**, 211 (1995); (c) A. Aneschi, D. Gatteschi, M.C. Melandri, P. Rey, R. Sessoli. *Inorg. Chem.*, **29**, 4228 (1990); (d) G. Wrzeszcz, L. Dobrzan'ska, A. Wojtczak, A. Grodzicki. *J. Chem. Soc., Dalton Trans.*, 2862 (2002).