Electronic Supplementary Information

Hexanuclear $Fe^{III}_2Co^{III}_2M^{II}_2$ (M = Cu, Ni, Mn) Clusters Based on Kläui's Tripodal Ligand and Tricyanometalates: Syntheses, Structures and Magnetic Properties

Ling-Chen Kang, Ming-Xia Yao, Xin Chen, Yi-Zhi Li, You Song, Jing-Lin Zuo* and Xiao-Zeng You

State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, P. R. China.

* To whom correspondence should be addressed. Email: zuojl@nju.edu.cn. Fax: +86-25-83314502. Nanjing University.

Table S1. Selected bond lengths (Å) and angles (deg) for **1**

Bond lengths			
Fe1–C1	1.924(4)	Fe1–C2	1.910(4)
Fe1–N8	1.962(3)	Fe1–C3	1.925(5)
Fe1–N6	1.987(3)	Fe1–N4	1.966(3)
Co1–P3	2.1507(14)	Co1–P1	2.1641(14)
Co1–P2	2.1684(17)	Cu1–N2	1.962(4)
Cu1–N1	1.972(4)	Cu1–O1	1.950(3)
Cu1–O7	1.978(3)	Cu1–O4	2.178(3)
C1–N1	1.132(6)	C2–N2#1	1.145(6)
C3–N3	1.131(6)		
Bond angles			
P3–Co1–P1	88.74(6)	P3–Co1–P2	90.32(6)
P1–Co1–P2	93.22(6)	O1–Cu1–N1	88.15(13)
O1–Cu1–N2	165.95(16)	O1–Cu1–O7	89.00(13)
N2–Cu1–N1	92.56(14)	N1–Cu1–O7	170.14(15)
N2–Cu1–O7	87.94(13)	N2–Cu1–O4	99.60(15)
O1–Cu1–O4	94.25(14)	O7–Cu1–O4	92.86(14)
N1–Cu1–O4	96.76(15)	N1–C1–Fe1	176.9(4)
N2#1–C2–Fe1	179.7(4)	N3–C3–Fe1	179.5(5)
C1–N1–Cu1	173.1(4)	C2#1–N2–Cu1	174.3(4)

Symmetry transformations used to generate equivalent atoms: #1 –x + 1, –y + 1, –z

Table S2. Selected bond lengths (Å) and angles (deg) for **2**

Bond lengths			
Fe1–C1	1.908(4)	Fe1–C2#1	1.906(4)
Fe1–C3	1.942(4)	Fe1–N4	2.008(3)
Fe1–N6	1.997(4)	Fe1–N8	1.992(3)
Co1–P3	2.1125(12)	Co1–P1	2.1572(12)
Co1–P2	2.1914(12)	Cu1–N1	1.983(3)
Cu1–N2	1.960(4)	Cu1–O1	2.116(3)
Cu1–O4	1.970(3)	Cu1–O7	1.944(3)
C1–N1	1.133(5)	C2–N2	1.165(5)
C3–N3	1.072(5)		
Bond angles			
P3–Co1–P1	94.15(5)	P3–Co1–P2	87.95(5)
P1–Co1–P2	87.94(12)	O1–Cu1–O4	95.75(11)
O1–Cu1–O7	94.29(11)	O4–Cu1–O7	87.94(12)
N1–Cu1–O1	96.12(13)	N1–Cu1–O4	89.71(13)
N1–Cu1–O7	169.50(13)	N2–Cu1–O1	99.91(12)
N2–Cu1–O4	163.93(13)	N2–Cu1–O7	87.30(13)
N1–Cu1–N2	92.20(14)	N1–C1–Fe1	177.9(4)

N2–C2–Fe1#1	178.8(3)	N3–C3–Fe1	177.3(4)
C1– N1–Cu1	172.3(3)	C2– N2–Cu1	172.8(3)

Symmetry transformations used to generate equivalent atoms: #1 –x + 1/2, –y + 1/2, z

Table S3. Selected bond lengths (Å) and angles (deg) for **3**

Bond lengths			
Fe1–C3	1.913(9)	Fe1–C2	1.913(7)
Fe1–N4	1.951(6)	Fe1–C1	1.931(7)
Fe1–N6	1.966(5)	Fe1–N8	1.958(6)
Co1–P3	2.155(2)	Co1–P1	2.156(2)
Co1–P2	2.162(2)	Cu1–N2	1.961(6)
Cu1–N1	1.969(6)	Cu1–O7	1.947(4)
Cu1–O1	1.948(5)	Cu1–O4	2.219(5)
C1–N1	1.131(8)	C2–N2#1	1.168(8)
C3–N3	1.148(10)		
Bond angles			
P3–Co1–P1	92.16(9)	P3–Co1–P2	92.18(9)
P1–Co1–P2	89.53(8)	O1–Cu1–O4	91.6(2)
O1–Cu1–O7	90.7(2)	O4–Cu1–O7	92.9(2)
N1–Cu1–O1	86.9(2)	N1–Cu1–O4	103.2(2)
N1–Cu1–O7	163.8(2)	N2–Cu1–O1	169.4(3)
N2–Cu1–O4	98.9(2)	N2–Cu1–O7	88.1(2)
N1–Cu1–N2	91.3(2)	N1–C1–Fe1	179.3(6)
N2#1–C2–Fe1	178.8(6)	N3–C3–Fe1	177.7(8)
C1– N1–Cu1	172.2(6)	C2#1– N2–Cu1	174.8(6)

Symmetry transformations used to generate equivalent atoms: #1 –x, –y, –z + 1

Table S4. Selected bond lengths (Å) and angles (deg) for **4**

Bond lengths			
Fe1–C1	1.916(5)	Fe1–C2	1.917(5)
Fe1–C3	1.929(5)	Fe1–N4	1.973(4)
Fe1–N6	1.976(4)	Fe1–N8	1.976(4)
Co(1)-P(3)	2.1566(17)	Co(1)-P(1)	2.1573(17)
Co(1)-P(2)	2.1596(18)	Ni1–N1	2.061(4)
Ni1–N2	2.046(4)	Ni1–N10	2.138(5)
Ni1–O1	2.034(3)	Ni1–O4	2.071(3)
Ni1–O7	2.053(3)	C1–N1	1.141(5)
C2–N2#1	1.142(6)	C3–N3	1.130(6)
Bond angles			
P3–Co1–P1	90.25(6)	P3–Co1–P2	89.78(6)
P1–Co1–P2	90.91(7)	O1–Ni1–O4	89.94(13)

O1–Ni1–O7	88.90(14)	O4–Ni1–O7	89.89(13)
N1–Ni1–O1	89.52(14)	N1–Ni1–O4	89.55(14)
N1–Ni1–O7	178.33(14)	N2–Ni1–O1	176.74(15)
N2–Ni1–O4	92.33(15)	N2–Ni1–O7	88.76(15)
N10–Ni1–O1	91.20(16)	N10–Ni1–O4	177.90(15)
N10–Ni1–O7	91.89(16)	N1–Ni1–N2	92.84(15)
N1–Ni1–N10	88.70(17)	N2–Ni1–N10	86.60(17)
N1–C1–Fe1	178.6(4)	N2#1–C2–Fe1	177.2(4)
N3–C3–Fe1	177.8(5)	C1–N1–Ni1	175.2(4)
C2#1–N2–Ni1	171.8(4)		

Symmetry transformations used to generate equivalent atoms: #1 –x + 1, –y + 1, –z

Table S5. Selected bond lengths (Å) and angles (deg) for **5**

Bond lengths			
Fe1–C1	1.906(8)	Fe1–C2	1.895(8)
Fe1–C3	1.907(8)	Fe1–N8	1.964(5)
Fe1–N6	1.964(6)	Fe1–N4	1.972(6)
Co1–P2	2.163(3)	Co1–P3	2.164(3)
Co1–P1	2.165(2)	Mn1–O4	2.130(5)
Mn1–O7	2.146(5)	Mn1–O1	2.160(5)
Mn1–N2	2.215(7)	Mn1–N1	2.218(7)
Mn1–N10	2.362(7)	C1–N1	1.152(8)
C2–N2#1	1.151(8)	C3–N3	1.150(8)
Bond angles			
P2–Co1–P3	90.79(10)	P2–Co1–P1	92.94(10)
P3–Co1–P1	89.85(10)	O4–Mn1–O7	88.69(19)
O4–Mn1–O1	85.8(2)	O7–Mn1–O1	88.5(2)
O4–Mn1–N2	171.2(2)	O7–Mn1–N2	97.7(2)
O1–Mn1–N2	88.3(2)	O4–Mn1–N1	90.9(2)
O7–Mn1–N1	95.9(2)	O1–Mn1–N1	174.5(2)
N2–Mn1–N1	94.5(2)	O4–Mn1–N10	89.7(2)
O7–Mn1–N10	174.5(2)	O1–Mn1–N10	86.2(2)
N2–Mn1–N10	83.4(2)	N1–Mn1–N10	89.4(2)
N1–C1–Fe1	177.6(7)	N2#1–C2–Fe1	177.0(7)
N3–C3–Fe1	175.9(7)	C1–N1–Mn1	172.3(6)
C2#1–N2–Mn1	168.9(6)		

Symmetry transformations used to generate equivalent atoms: #1 –x + 1, –y + 2, –z + 2

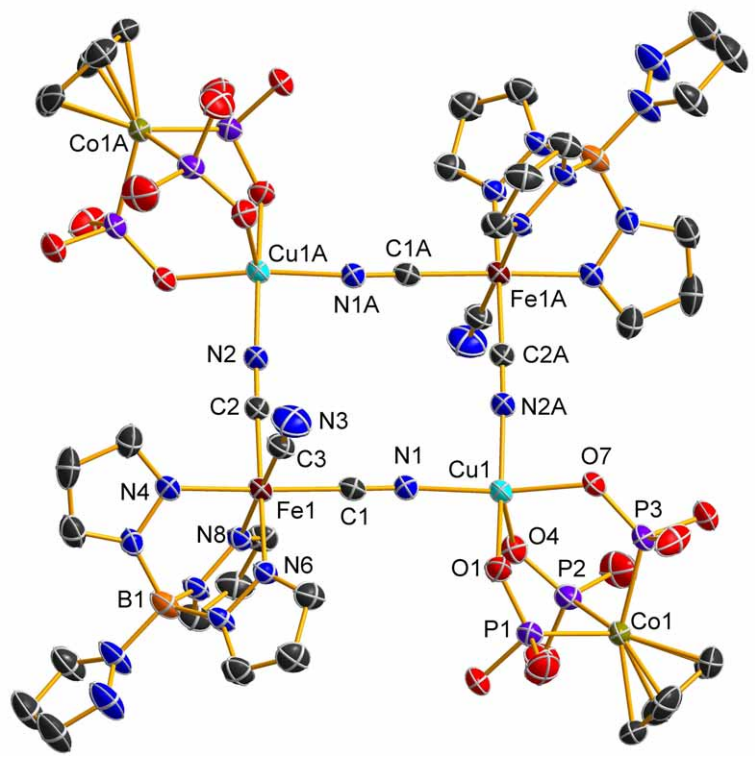


Fig. S1 ORTEP view of the neutral hexanuclear cluster of **3** with an atom-numbering scheme at the 30% probability level. Ethyl groups of the phosphates and H atoms are omitted for clarity.

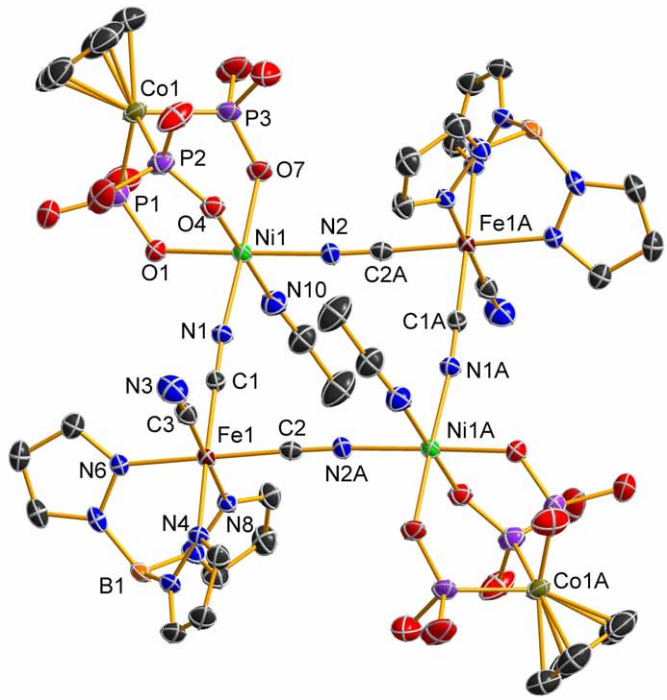


Fig. S2 ORTEP view of the neutral hexanuclear clusters of **4** with an atom-numbering scheme at the 30% probability level. Ethyl groups of the phosphates and H atoms are omitted for clarity.

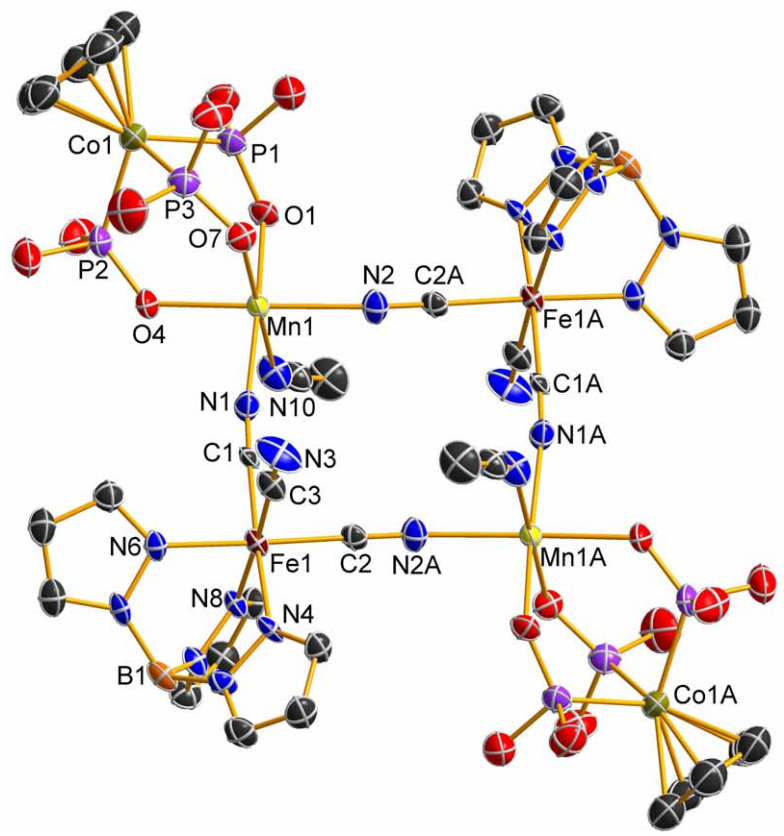
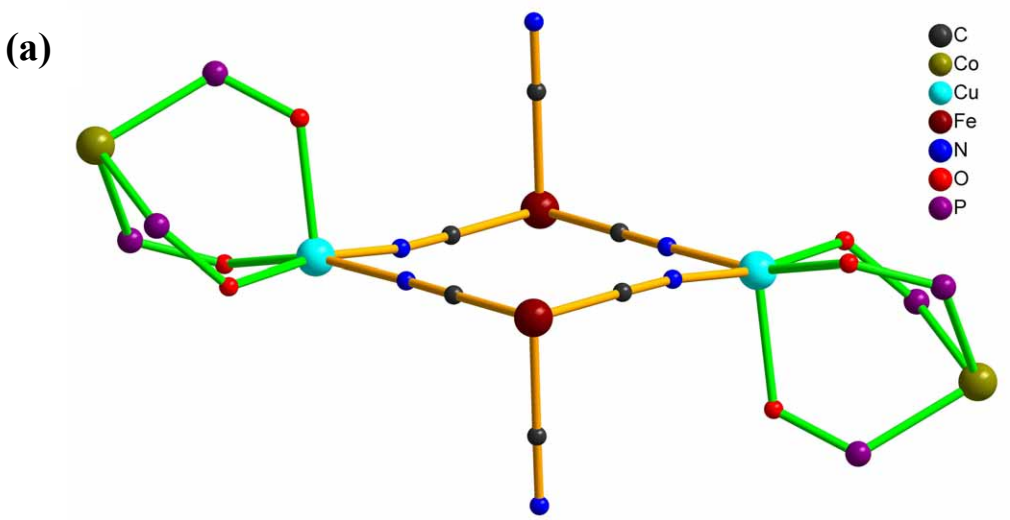


Fig. S3 ORTEP view of the neutral hexanuclear clusters of **5** with an atom-numbering scheme at the 30% probability level. Ethyl groups of the phosphates and H atoms are omitted for clarity.



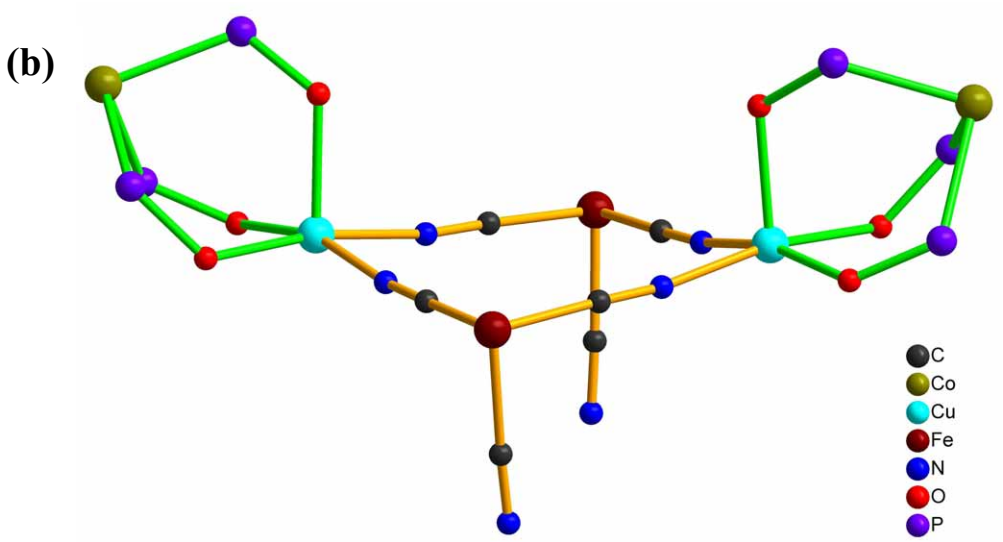


Fig. S4 **(a)** A view to show the *trans* conformation of the L_{CoEt} units in complex **1**. **(b)** A view to show the *cis* conformation of the L_{CoEt} units in complex **2**.

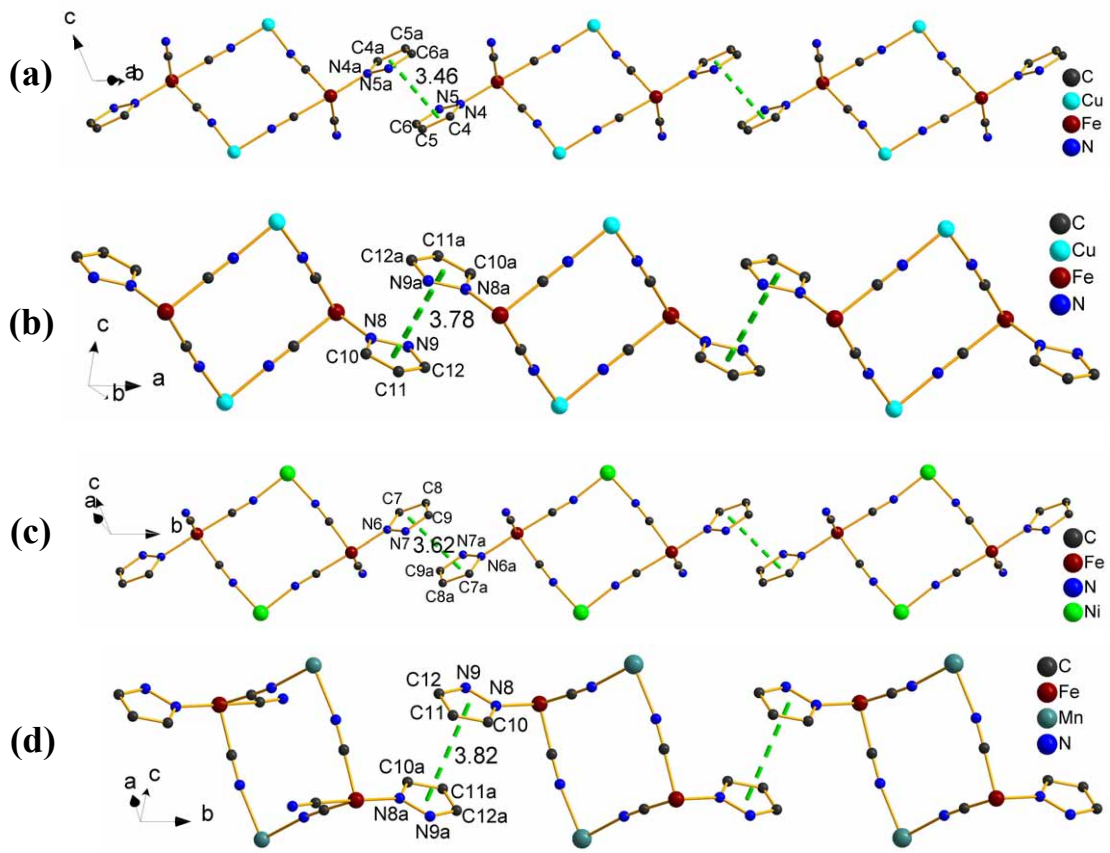


Fig. S5 A view to show the chains formed by π–π interactions (green dash lines) of the nearby pyrazole rings in complexes **1** (**a**), **3** (**b**), **4** (**c**) and **5** (**d**).

Table S6. Centroid distances of π–π stacking interactions between the pyrazole rings of complexes **1**, **3**, **4** and **5**.

Complexes	**1**	**3**	**4**	**5**
Centroid distances (Å)	3.4604(7)	3.7772(7)	3.6229(10)	3.8232(14)

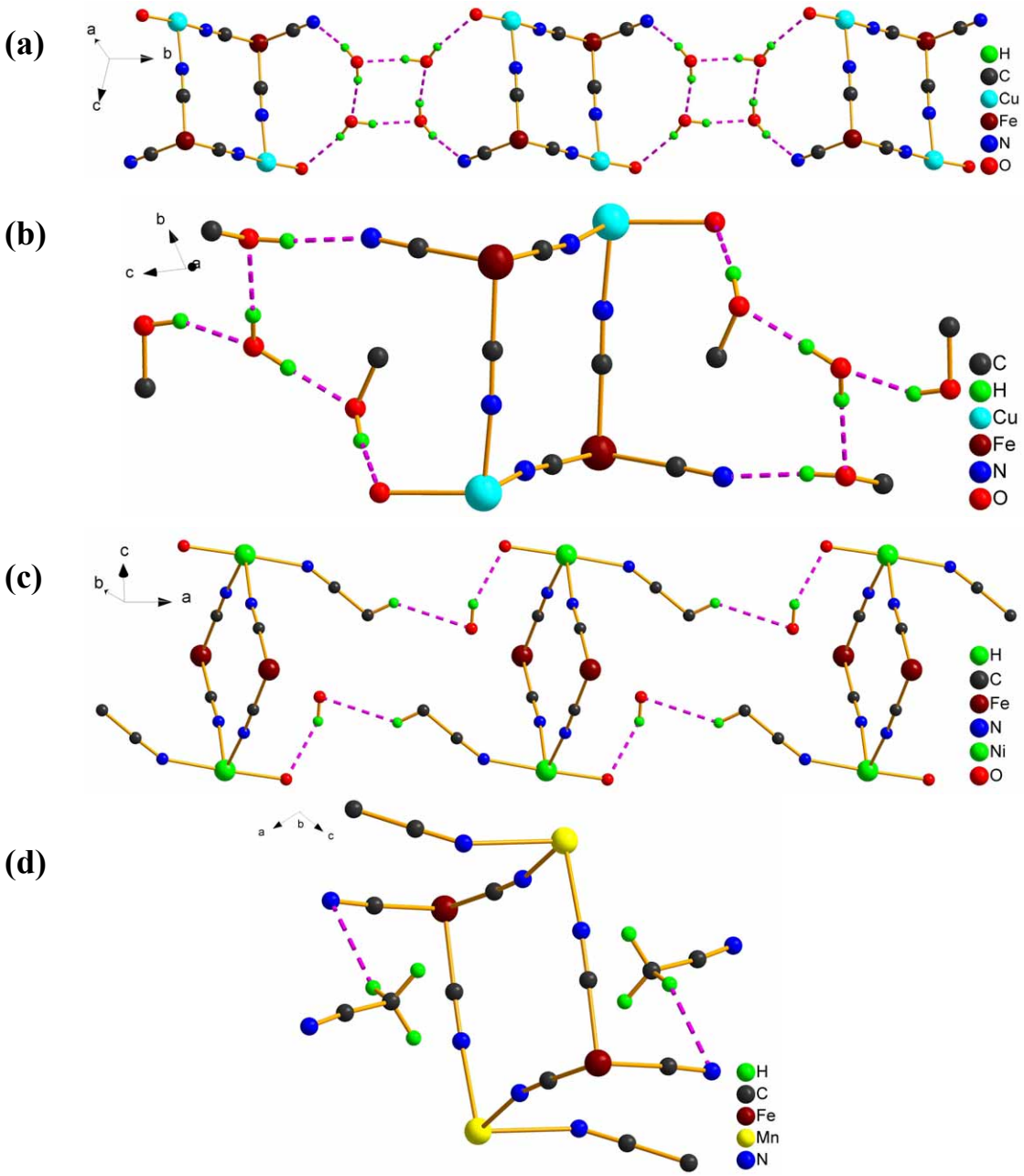


Fig. S6 A view to show the hydrogen-bond interactions (pink dash lines) within complexes **1** (**a**), **3** (**b**), **4** (**c**) and **5** (**d**).