Supporting Information

Three-Dimensional Fe^{II}-$[Mo^{III}(CN)_7]^{4-}$ Magnets with Ordering below 65 K and Distinct Topologies Induced by Cation Identity

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Table S1 Selected bond lengths (Å) and angles (°) for **1-2**

1: {[$Fe_2(H_2O)_5[Mo(CN)_7]\cdot 5H_2O$}$_n$					
Bond lengths [Å]					
Mo(1)-C(4)	2.102(16)	Fe(1)-N(2)#1	2.06(2)	Fe(2)-N(5)#1	2.095(13)
Mo(1)-C(5)	2.100(17)	Fe(1)-O(1)	2.142(12)	Fe(2)-N(7)#3	2.109(11)
Mo(1)-C(3)	2.123(18)	Fe(1)-N(1)	2.128(17)	Fe(2)-N(4)#4	2.139(15)
Mo(1)-C(1)	2.160(16)	Fe(1)-O(3)	2.136(14)	Fe(2)-O(5)	2.155(15)
Mo(1)-C(6)	2.190(19)	Fe(1)-N(3)#2	2.152(17)	Fe(2)-O(4)	2.279(11)
Mo(1)-C(2)	2.19(2)	Fe(1)-O(2)	2.21(2)		
Mo(1)-C(7)	2.207(13)	Fe(2)-N(6)	2.087(18)		
Bond angles					
C(4)-Mo(1)-C(5)	74.3(9)	N(2)#1-Fe(1)-N(1)	94.0(6)	N(7)#3-Fe(2)-O(5)	84.6(7)
C(4)-Mo(1)-C(3)	72.3(7)	O(1)-Fe(1)-N(1)	91.5(5)	N(4)#4-Fe(2)-O(5)	81.8(7)
C(5)-Mo(1)-C(3)	114.7(8)	N(2)#1-Fe(1)-O(3)	87.1(8)	N(6)-Fe(2)-O(4)	174.0(6)
C(4)-Mo(1)-C(1)	123.4(9)	O(1)-Fe(1)-O(3)	176.2(5)	N(5)#1-Fe(2)-O(4)	83.2(5)
C(5)-Mo(1)-C(1)	161.1(8)	N(1)-Fe(1)-O(3)	90.2(7)	N(7)#3-Fe(2)-O(4)	81.7(7)
C(3)-Mo(1)-C(1)	79.9(7)	N(2)#1-Fe(1)-N(3)#2	166.4(9)	N(4)#4-Fe(2)-O(4)	87.4(7)
C(4)-Mo(1)-C(6)	73.7(10)	O(1)-Fe(1)-N(3)#2	90.5(6)	O(5)-Fe(2)-O(4)	93.2(6)
C(5)-Mo(1)-C(6)	93.6(4)	N(1)-Fe(1)-N(3)#2	97.7(8)	N(1)-C(1)-Mo(1)	175.8(17)
C(3)-Mo(1)-C(6)	126.8(10)	O(3)-Fe(1)-N(3)#2	86.0(7)	N(2)-C(2)-Mo(1)	176.6(19)
C(1)-Mo(1)-C(6)	86.1(7)	N(2)#1-Fe(1)-O(2)	82.3(10)	N(3)-C(3)-Mo(1)	178(2)
C(4)-Mo(1)-C(2)	125.9(10)	O(1)-Fe(1)-O(2)	89.5(8)	N(4)-C(4)-Mo(1)	176(3)
C(5)-Mo(1)-C(2)	82.2(7)	N(1)-Fe(1)-O(2)	176.3(8)	N(5)-C(5)-Mo(1)	176.4(16)
C(3)-Mo(1)-C(2)	74.8(8)	O(3)-Fe(1)-O(2)	88.9(9)	N(6)-C(6)-Mo(1)	174(2)
C(1)-Mo(1)-C(2)	90.7(6)	N(3)#2-Fe(1)-O(2)	85.8(8)	N(7)-C(7)-Mo(1)	178.2(19)
C(6)-Mo(1)-C(2)	156.9(8)	N(6)-Fe(2)-N(5)#1	90.8(5)	C(1)-N(1)-Fe(1)	173.3(18)
C(4)-Mo(1)-C(7)	138.6(4)	N(6)-Fe(2)-N(7)#3	99.8(8)	C(2)-N(2)-Fe(1)#5	179(2)
C(5)-Mo(1)-C(7)	77.8(8)	N(5)#1-Fe(2)-N(7)#3	97.3(8)	C(3)-N(3)-Fe(1)#6	154(2)
C(3)-Mo(1)-C(7)	148.4(7)	N(6)-Fe(2)-N(4)#4	92.5(8)	C(4)-N(4)-Fe(2)#3	158.8(15)
C(1)-Mo(1)-C(7)	83.7(6)	N(5)#1-Fe(2)-N(4)#4	95.5(8)	C(5)-N(5)-Fe(2)#5	172.1(13)
C(6)-Mo(1)-C(7)	78.3(8)	N(7)#3-Fe(2)-N(4)#4	162.1(5)	C(6)-N(6)-Fe(2)	172.7(19)
C(2)-Mo(1)-C(7)	78.6(7)	N(6)-Fe(2)-O(5)	92.7(8)	C(7)-N(7)-Fe(2)#4	173.3(16)
N(2)#1-Fe(1)-O(1)	96.1(8)	N(5)#1-Fe(2)-O(5)	175.7(8)		
Symmetry transformations used to generate equivalent atoms: #1 x+1,y,z #2 -x+2,y+1/2,-z+1 #3 -x+2,y-1/2,-z #4 -x+2,y+1/2,-z #5 x-1,y,z #6 -x+2,y-1/2,-z+1					

2: {[$NH_2(CH_3)_2]_2[Fe_5(H_2O)_{10}[Mo(CN)_7]_3]\cdot 8H_2O$}$_n$					
Bond lengths [Å]					
Mo(1)-C(6)	2.113(8)	Mo(2)-C(11)#2	2.150(8)	Fe(2)-N11	2.140(7)
Mo(1)-C(5)	2.140(7)	Mo(2)-C(11)	2.150(8)	Fe(2)-N(1)#6	2.149(7)
Mo(1)-C(7)	2.141(8)	Mo(2)-C(8)	2.192(11)	Fe(2)-O(3)	2.188(6)
Mo(1)-C(4)	2.149(9)	Fe(1)-N(10)	2.090(10)	Fe(2)-O(4)	2.205(6)

Mo(1)-C(3)	2.156(8)	Fe(1)-N(5)	2.119(7)	Fe(3)-N(4)#3	2.081(7)
Mo(1)-C(1)	2.175(8)	Fe(1)-N(5)#2	2.119(7)	Fe(3)-N(6)#1	2.099(8)
Mo(1)-C(2)	2.180(8)	Fe(1)-O(1)	2.120(9)	Fe(3)-N(9)	2.100(7)
C(12)-Mo(2)	2.125(12)	Fe(1)-N(12)#7	2.175(10)	Fe(3)-N(2)#4	2.101(7)
Mo(2)-C(10)	2.120(12)	Fe(1)-O(2)	2.264(9)	Fe(3)-O(5)	2.241(7)
Mo(2)-C(9)#2	2.137(8)	Fe(2)-N(7)#2	2.102(7)	Fe(3)-O(6)	2.262(8)
Mo(2)-C(9)	2.137(8)	Fe(2)-N(3)#5	2.133(7)		
Bond angles					
C(10)-Mo(2)-C(12)	73.0(4)	C(3)-Mo(1)-C(1)	88.8(3)	N11-Fe(2)-O(4)	88.7(3)
C(10)-Mo(2)-C(9)#2	124.2(3)	C(6)-Mo(1)-C(2)	149.0(3)	N(1)#6-Fe(2)-O(4)	85.3(3)
C(12)-Mo(2)-C(9)#2	76.4(3)	C(5)-Mo(1)-C(2)	140.2(3)	O(3)-Fe(2)-O(4)	87.2(2)
C(10)-Mo(2)-C(9)	124.2(3)	C(7)-Mo(1)-C(2)	81.1(3)	N(10)-Fe(1)-N(5)	90.8(2)
C(12)-Mo(2)-C(9)	76.4(3)	C(4)-Mo(1)-C(2)	73.8(3)	N(10)-Fe(1)-N(5)#2	90.8(2)
C(9)#2-Mo(2)-C(9)	91.1(4)	C(3)-Mo(1)-C(2)	79.6(3)	N(5)-Fe(1)-N(5)#2	172.7(5)
C(10)-Mo(2)-C(11)#2	78.4(3)	C(1)-Mo(1)-C(2)	79.1(3)	N(10)-Fe(1)-O(1)	96.5(4)
C(12)-Mo(2)-C(11)#2	124.2(3)	N(4)#3-Fe(3)-N(6)#1	92.1(3)	N(5)-Fe(1)-O(1)	86.4(2)
C(9)#2-Mo(2)-C(11)#2	155.2(3)	N(4)#3-Fe(3)-N(9)	165.6(3)	N(5)#2-Fe(1)-O(1)	86.4(2)
C(9)-Mo(2)-C(11)#2	82.0(3)	N(6)#1-Fe(3)-N(9)	93.8(3)	N(10)-Fe(1)-N(12)#7	164.6(4)
C(10)-Mo(2)-C(11)	78.4(3)	N(4)#3-Fe(3)-N(2)#4	97.1(3)	N(5)-Fe(1)-N(12)#7	90.2(2)
C(12)-Mo(2)-C(11)	124.2(3)	N(6)#1-Fe(3)-N(2)#4	91.6(3)	N(5)#2-Fe(1)-N(12)#7	90.2(2)
C(9)#2-Mo(2)-C(11)	82.0(3)	N(9)-Fe(3)-N(2)#4	95.8(3)	O(1)-Fe(1)-N(12)#7	98.9(4)
C(9)-Mo(2)-C(11)	155.2(3)	N(4)#3-Fe(3)-O(5)	83.5(3)	N(10)-Fe(1)-O(2)	82.7(4)
C(11)#2-Mo(2)-C(11)	94.4(4)	N(6)#1-Fe(3)-O(5)	97.0(3)	N(5)-Fe(1)-O(2)	93.6(2)
C(10)-Mo(2)-C(8)	143.9(4)	N(9)-Fe(3)-O(5)	82.8(3)	N(5)#2-Fe(1)-O(2)	93.6(2)
C(10)-Mo(2)-C(12)	73.0(4)	C(3)-Mo(1)-C(1)	88.8(3)	O(1)-Fe(1)-O(2)	179.2(4)
C(12)-Mo(2)-C(8)	143.1(4)	C(6)-Mo(1)-C(2)	149.0(3)	N(12)#7-Fe(1)-O(2)	81.9(4)
C(9)#2-Mo(2)-C(8)	78.0(3)	N(2)#4-Fe(3)-O(5)	171.4(3)	C(10)-N(10)-Fe(1)	172.7(10)
C(9)-Mo(2)-C(8)	78.0(3)	N(4)#3-Fe(3)-O(6)	93.2(3)	C(1)-N(1)-Fe(2)#8	173.7(6)
C(11)#2-Mo(2)-C(8)	77.3(3)	N(6)#1-Fe(3)-O(6)	173.5(4)	C(7)-N(7)-Fe(2)#2	177.5(7)
C(11)-Mo(2)-C(8)	77.3(3)	N(9)-Fe(3)-O(6)	81.8(3)	C(11)-N11-Fe(2)	171.3(7)
C(6)-Mo(1)-C(5)	70.8(3)	N(2)#4-Fe(3)-O(6)	84.1(3)	C(9)-N(9)-Fe(3)	169.7(7)
C(6)-Mo(1)-C(7)	112.5(3)	O(5)-Fe(3)-O(6)	87.2(3)	C(3)-N(3)-Fe(2)#9	175.7(7)
C(5)-Mo(1)-C(7)	79.0(3)	N(7)#2-Fe(2)-N(3)#5	93.7(3)	C(5)-N(5)-Fe(1)	174.0(8)
C(6)-Mo(1)-C(4)	129.0(3)	N(7)#2-Fe(2)-N11	89.4(3)	C(6)-N(6)-Fe(3)#7	167.0(7)

C(5)-Mo(1)-C(4)	74.4(3)	N(3)#5-Fe(2)-N11	174.2(3)	C(2)-N(2)-Fe(3)#4	175.3(7)
C(7)-Mo(1)-C(4)	95.7(3)	N(7)#2-Fe(2)-N(1)#6	97.7(3)	C(4)-N(4)-Fe(3)#10	162.0(8)
C(6)-Mo(1)-C(3)	81.3(3)	N(3)#5-Fe(2)-N(1)#6	90.1(3)	C(12)-N(12)-Fe(1)#1	142.7(9)
C(5)-Mo(1)-C(3)	121.2(3)	N11-Fe(2)-N(1)#6	94.4(3)	N(7)-C(7)-Mo(1)	175.7(7)
C(7)-Mo(1)-C(3)	159.2(3)	N(7)#2-Fe(2)-O(3)	89.7(3)	N(3)-C(3)-Mo(1)	175.5(7)
C(4)-Mo(1)-C(3)	86.2(3)	N(3)#5-Fe(2)-O(3)	89.3(2)	N(10)-C(10)-Mo(2)	179.7(10)
C(6)-Mo(1)-C(1)	76.2(3)	N11-Fe(2)-O(3)	85.8(2)	N(8)-C(8)-Mo(2)	179.3(11)
C(5)-Mo(1)-C(1)	129.9(3)	N(1)#6-Fe(2)-O(3)	172.6(3)	N(5)-C(5)-Mo(1)	177.7(9)
C(7)-Mo(1)-C(1)	80.1(3)	N(7)#2-Fe(2)-O(4)	176.5(3)	N11-C(11)-Mo(2)	175.6(7)
C(4)-Mo(1)-C(1)	152.9(3)	N(3)#5-Fe(2)-O(4)	88.0(3)	N(12)-C(12)-Mo(2)	173.3(10)
N(6)-C(6)-Mo(1)	176.2(8)	N(4)-C(4)-Mo(1)	178.6(8)	N(2)-C(2)-Mo(1)	175.2(7)
N(1)-C(1)-Mo(1)	176.6(7)	N(9)-C(9)-Mo(2)	175.5(7)		

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,y,-z+1/2 #2 x,-y+1/2,z #3 x+1,y,z
#4 -x+1,-y,-z+1 #5 -x+1/2,y+1/2,z+1/2
#6 -x+1,y+1/2,-z+1 #7 x-1/2,y,-z+1/2
#8 -x+1,y-1/2,-z+1 #9 -x+1/2,y-1/2,z-1/2
#10 x-1,y,z

Table S2. Analysis results by Contiouous Shape Measures (CShM)

Mo							
Shape	Heptagon	Hexagonal pyramid	Pentagonal bipyramid	Capped octahedron	**Capped trigonal prism**	Johnson pentagonal bipyramid	Elongated triangular pyramid
Mo1 of **1**	32.778	21.374	5.024	1.586	**0.475**	8.414	20.628
Mo1 of **2**	32.789	21.626	4.208	1.493	**0.658**	7.766	19.476
Mo2 of **2**	33.296	21.062	6.490	1.559	**0.188**	10.063	20.995

Fe					
Shape	Hexagon	Pentagonal	**Octahedro**	Trigonal	Johnson pentagonal pyramid

		pyramid	n	prism	
Fe1 of **1**	33.016	26.824	**0.360**	13.688	30.592
Fe2 of **1**	31.753	24.109	**0.772**	12.777	27.658
Fe1 of **2**	33.417	26.312	**0.685**	13.829	29.915
Fe2 of **2**	32.251	28.788	**0.145**	15.901	32.228
Fe3 of **2**	32.145	25.916	**0.598**	13.266	29.096

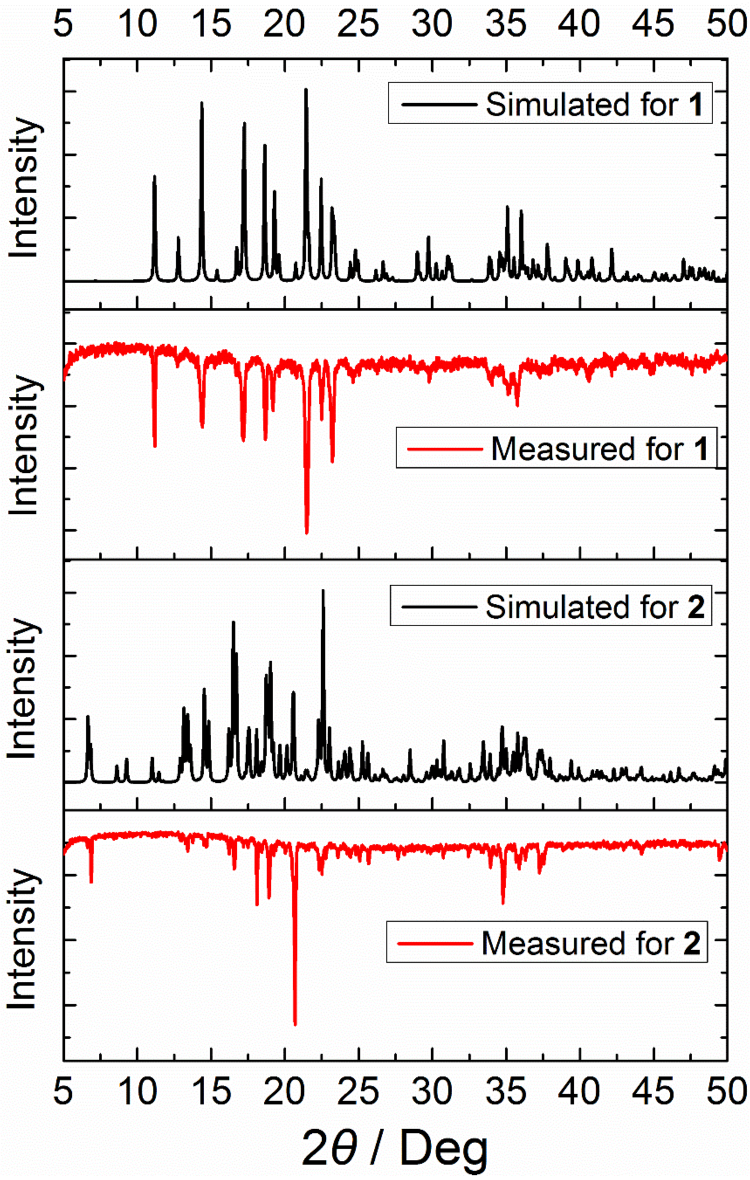

Figure S1. Experimental and calculated powder X-ray diffraction patterns for **1** and **2**.

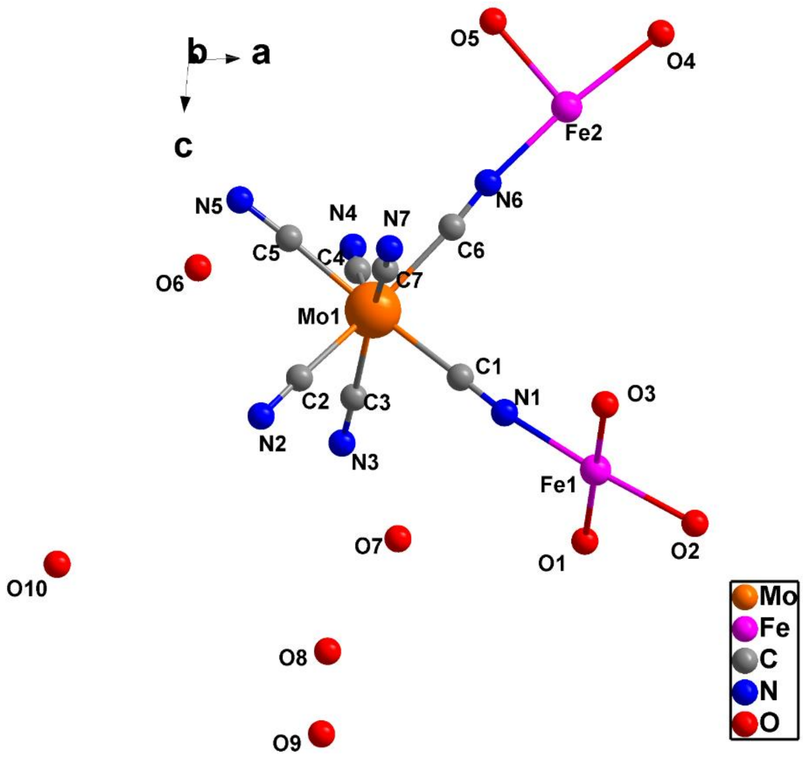

Figure S2. The asymmetric unit of **1**

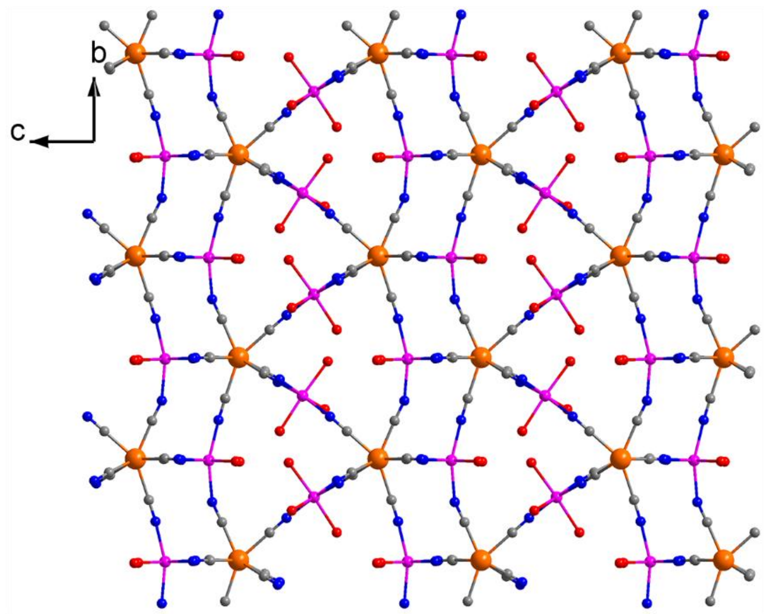

Figure S3. Global view of the crystal structure of **1** in the *bc* plane.

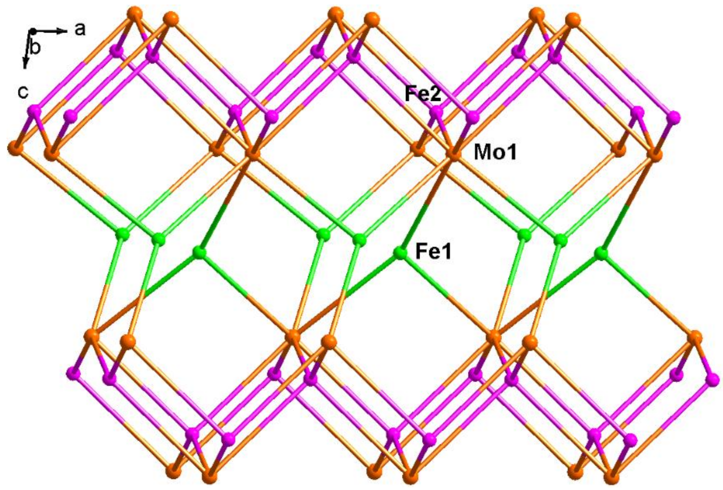

Figure S4. Schematic view of the 3,4,7-connected topology of **1**.

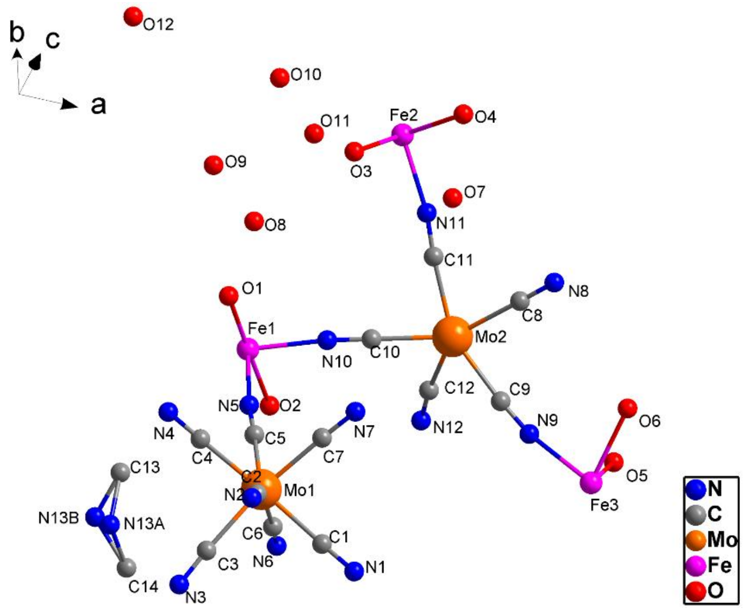

Figure S5. The asymmetric unit of **2**

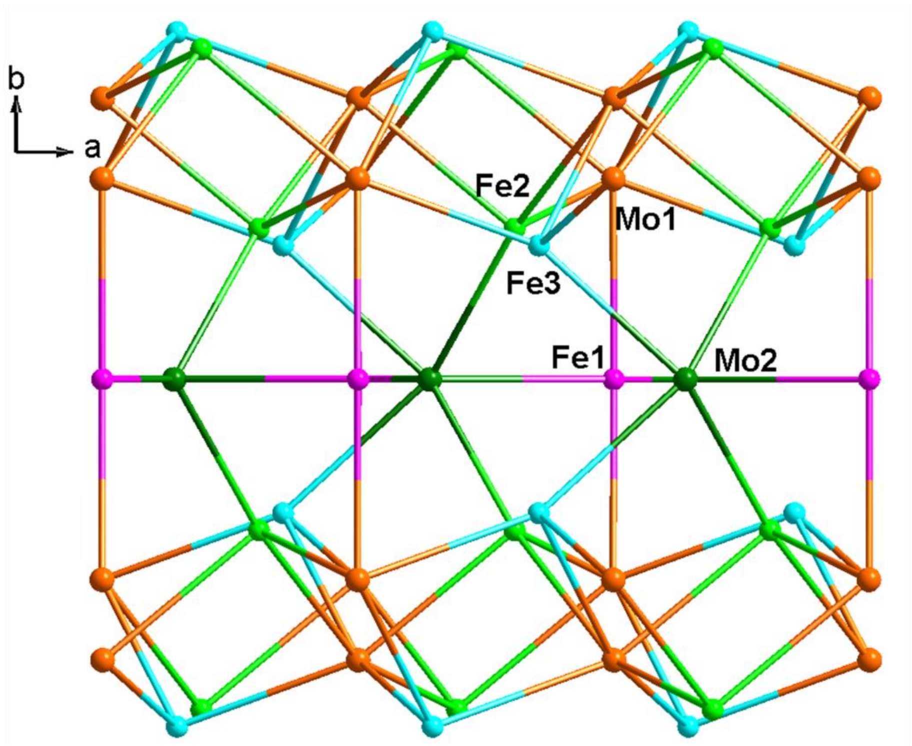

Figure S6. Schematic view of the 4,4,4,6,7-connected topology of **2**.

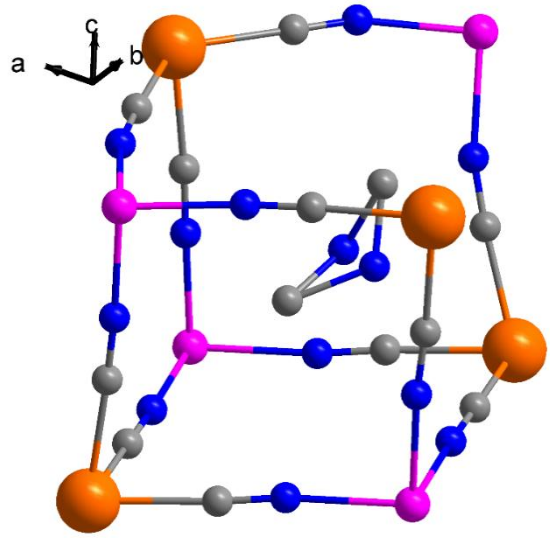

Figure S7. Fragment of the structure showing the cavity containing two-fold disordered $[NH_2(CH_3)_2]^+$ in the center.

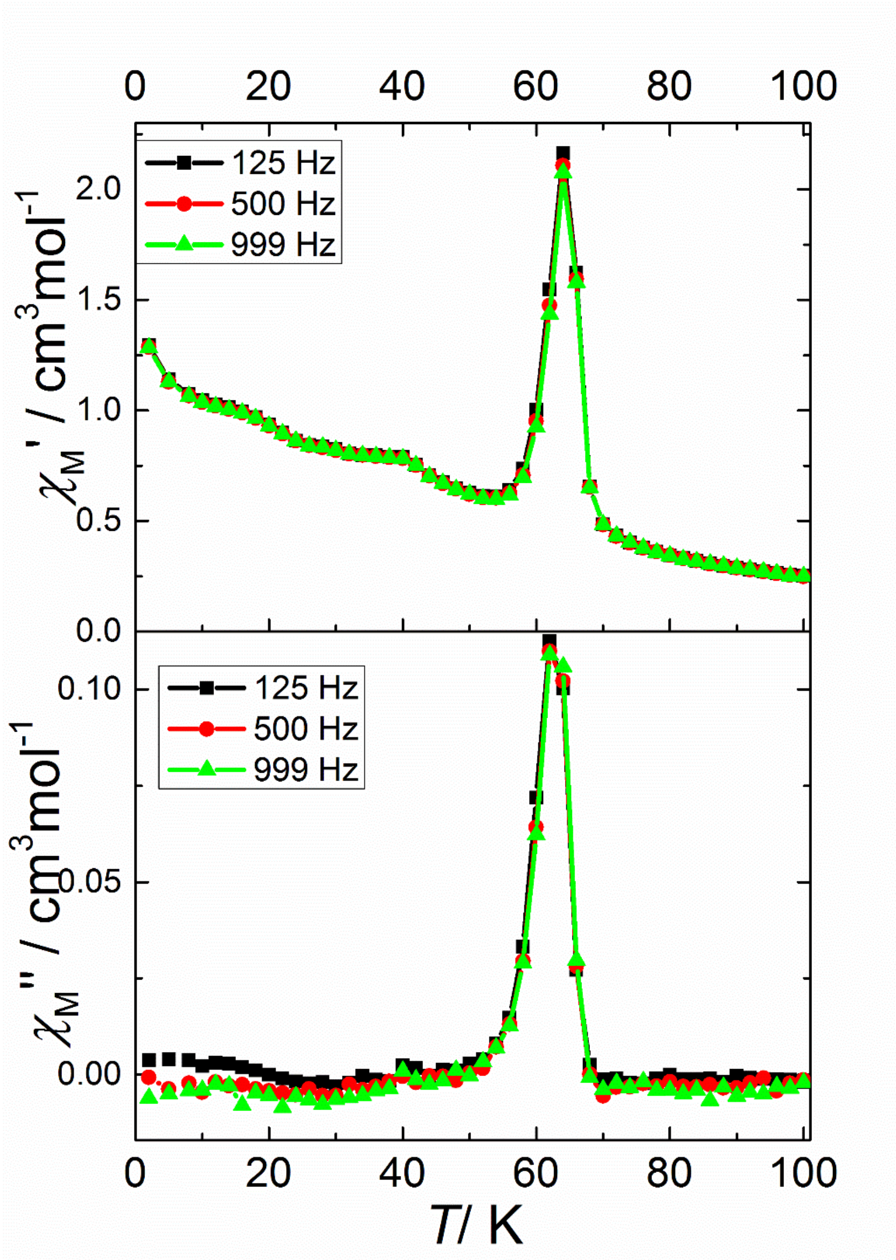

Figure S8. Temperature dependent ac susceptibility of **2** at different frequencies under H_{dc} = 0 Oe and H_{ac} = 2 Oe.

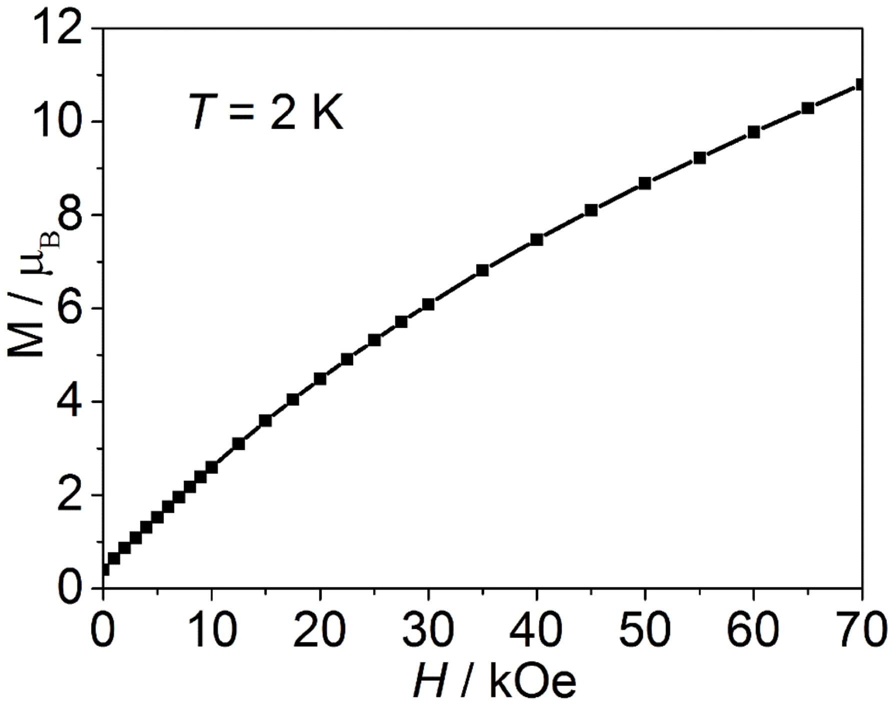

Figure S9. Field dependent magnetization of **2** measured at 2K.

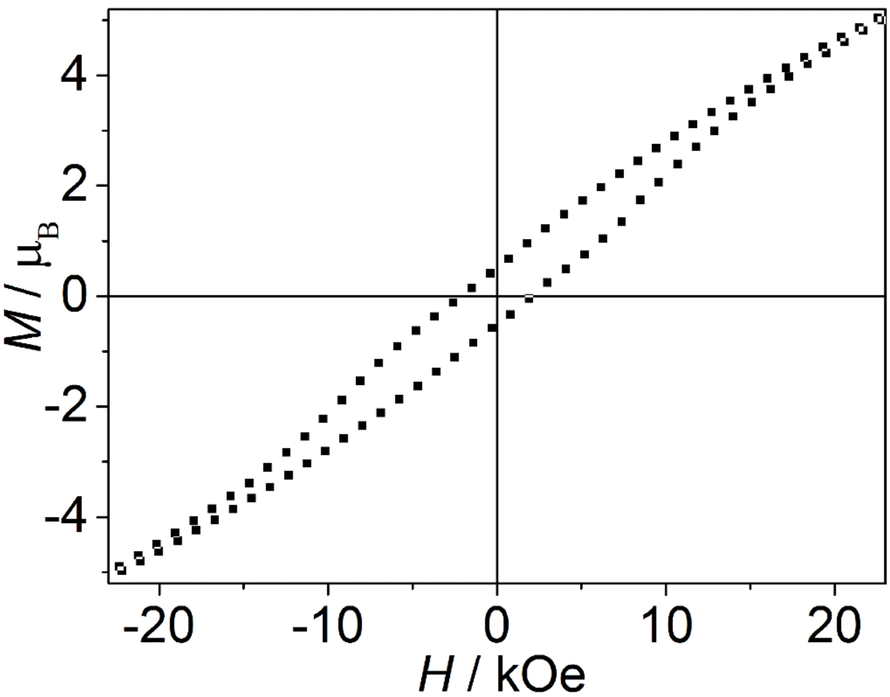

Figure S10. The hysteresis loop of **2** measured at 2K.