Supporting Information

22-Azametallacrown-8 complex with triazole-bridged ligand: synthesis, structure and magnetic properties

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Contents:

X-ray Crystallography.

Single-crystal X-ray diffraction data for complex **1**were collected on a Bruker Smart CCD area-detector diffractometer with Mo Kα radiation (λ = 0.71073 Å) by ω-scan mode operating at room temperature. The program *SAINT* was used for integration of the diffraction profiles, and semiempirical absorption corrections were applied using *SADABS*.[1,2] All of the structures were solved by direct methods using the *SHELXS* program of the *SHELXTL* package and refined by full-matrix least-squares methods with *SHELXL*.[3] Metal ions were located from the *E* maps, and the other non-H atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. Generally, C-bound H atoms were determined theoretically and refined with isotropic thermal parameters riding on their parents. H atoms of OH and DMF were first located by difference Fourier *E* maps and then treated isotropically as riding.

1. SAINT v5.0-6.01; Bruker Analytical X-ray Systems Inc.:Madison, WI, 1998.

2. Sheldrick, G. M.SADABS; University of Göttingen: Göttingen, Germany.

3. SHELXTL v5.1, Bruker Analytical X-ray Systems Inc.: Madison, WI, 1999.

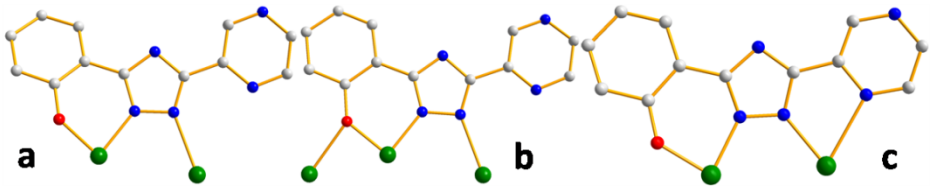

Fig. S1 The coordination modes of L ligands: (a), μ_2:η^1:η^1:η^1; (b), μ_3:η^2:η^1:η^1, (c), μ_2:η^1:η^1:η^1:η^1

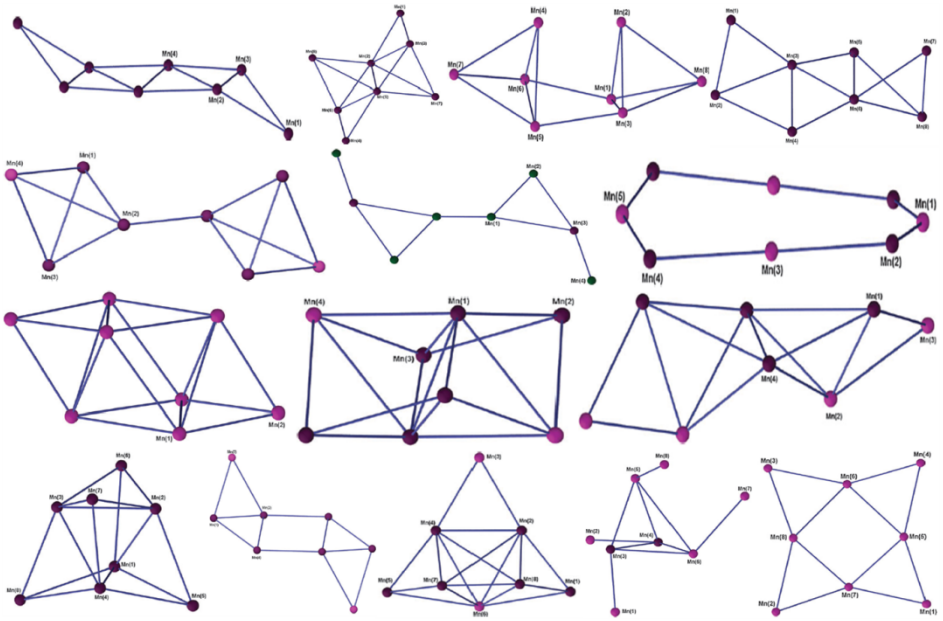

Fig. S2 Mn8 metal topologies

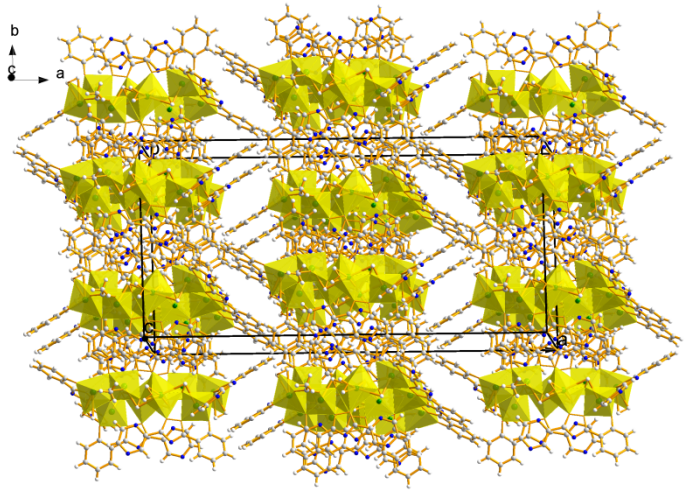

Fig. S3 The 3D packing arrangement formed through C–H···N, C–H···π and π···π interactions

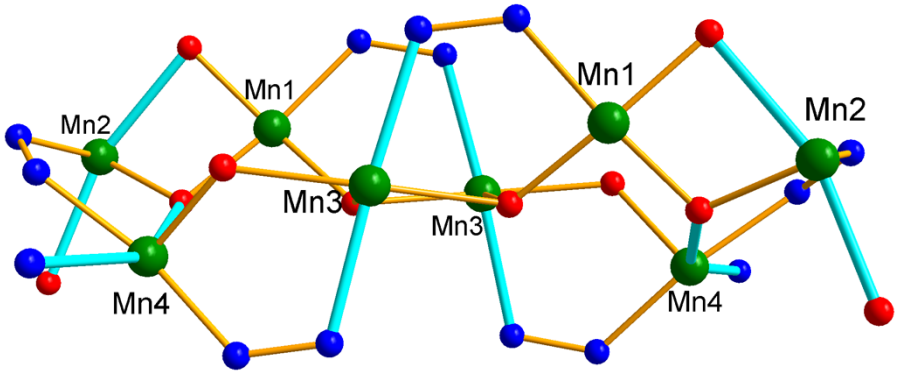

Fig. S4 The Jahn-Teller axes of Mn^{III} centers with sky blue.

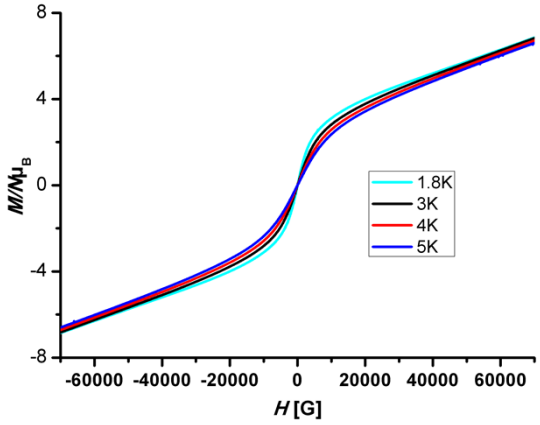

Fig. S5 Plots of isothermal magnetization, *M*, *vs*. field, *H*, for **1** at temperatures of between 1.8 K and 8 K.

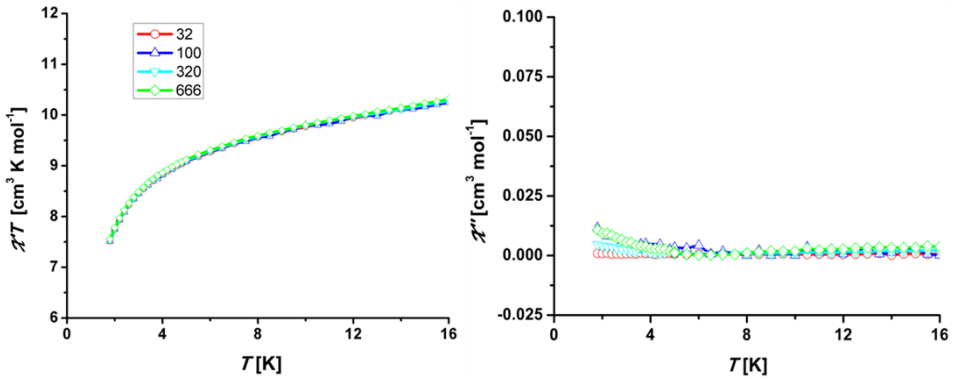

Fig. S6 In-phase of AC χ'_M *T vs T* plots (left panel) and out-of-phase χ''_M vs *T* plots (right panel) in the 1.8-16 K range with DC = 0 Oe.

Table S1. Crystal data and structure refinement for the complex **1**.

	1
Empirical formula	$C_{76}H_{60}Mn_8N_{30}O_{20}$
Formula weight	2153.06
Crystal system	Monoclinic
space group	*C2/c*
a (Å)	37.600(3)
b (Å)	18.2991(17)
c (Å)	14.1600(12)
α (°)	90
β (°)	101.491(2)
γ (°)	90
V (Å^3)	9547.5(14)
Z	4
ρ (Mg/m^3)	1.498
Absorption coefficient(mm^{-1})	1.102
F(000)	4344
Crystal size (mm^3)	0.13 × 0.12 × 0.11
Theta range for data collection	2.67 to 25.02 °
Reflections collected / unique	22432 / 8418 [R_{int} = 0.1154]
Completeness to *θ*	99.8 %
Max. and min. transmission	0.8884 and 0.8700
Data / restraints / parameters	8418 / 0 / 605
Goodness-of-fit on F^2	1.000
R_1 ($I > 2\sigma$(I))	0.0820
wR_2 ($I > 2\sigma$(I))	0.1798
R_1 (all data)	0.1605
wR_2 (all data)	0.2025

Table S2. Selected bond distances (Å) and angles (°) for complex **1**.

Mn(1)-O(6)	1.843(5)	Mn(3)-O(7)#1	2.118(5)
Mn(1)-O(7)	1.889(5)	Mn(3)-O(10)	2.210(7)
Mn(1)-O(1)	1.894(5)	Mn(3)-N(12)	2.303(6)
Mn(1)-N(1)	1.981(7)	Mn(3)-N(2)#1	2.311(6)
Mn(1)-O(4)	2.125(5)	Mn(3)-O(7)	2.361(5)
Mn(2)-O(6)	1.868(5)	Mn(4)-O(9)	1.854(5)
Mn(2)-O(2)	1.873(6)	Mn(4)-O(3)	1.875(6)

Mn(2)-N(6)	1.972(7)	Mn(4)-N(11)	1.990(6)
Mn(2)-O(5)	1.977(6)	Mn(4)-N(7)	2.038(7)
Mn(2)-O(8)	2.236(6)	Mn(4)-O(6)	2.154(5)
Mn(2)-O(1)	2.326(6)	Mn(4)-N(9)	2.511(6)
Mn(3)-O(9)	2.082(5)		
Mn(1)···Mn(2)	2.9408(17)	Mn(2)···Mn(4)	3.5040(19)
Mn(1)···Mn(3)	3.5180(18)	Mn(3)···Mn(2)	5.7441(18)
Mn(1)···Mn(4)	3.4331(16)	Mn(3)···Mn(3)#1	3.4391(17)
O(6)-Mn(1)-O(7)	94.6(2)	O(5)-Mn(2)-Mn(1)	79.83(17)
O(6)-Mn(1)-O(1)	85.5(2)	O(8)-Mn(2)-Mn(1)	122.39(16)
O(7)-Mn(1)-O(1)	167.1(2)	O(1)-Mn(2)-Mn(1)	40.06(14)
O(6)-Mn(1)-N(1)	173.0(2)	O(9)-Mn(3)-O(7)#1	162.9(2)
O(7)-Mn(1)-N(1)	88.7(2)	O(9)-Mn(3)-O(10)	102.7(2)
O(1)-Mn(1)-N(1)	89.9(2)	O(7)#1-Mn(3)-O(10)	94.4(2)
O(6)-Mn(1)-O(4)	92.9(2)	O(9)-Mn(3)-N(12)	82.4(2)
O(7)-Mn(1)-O(4)	96.8(2)	O(7)#1-Mn(3)-N(12)	96.8(2)
O(1)-Mn(1)-O(4)	96.0(2)	O(10)-Mn(3)-N(12)	90.5(2)
N(1)-Mn(1)-O(4)	92.8(2)	O(9)-Mn(3)-N(2)#1	100.8(2)
O(6)-Mn(1)-Mn(2)	37.87(16)	O(7)#1-Mn(3)-N(2)#1	80.6(2)
O(7)-Mn(1)-Mn(2)	131.25(16)	O(10)-Mn(3)-N(2)#1	87.3(2)
O(1)-Mn(1)-Mn(2)	52.22(17)	N(12)-Mn(3)-N(2)#1	176.4(2)
N(1)-Mn(1)-Mn(2)	139.80(19)	O(9)-Mn(3)-O(7)	84.0(2)
O(4)-Mn(1)-Mn(2)	80.21(15)	O(7)#1-Mn(3)-O(7)	79.0(2)
O(6)-Mn(2)-O(2)	172.8(2)	O(10)-Mn(3)-O(7)	169.6(2)
O(6)-Mn(2)-N(6)	89.0(3)	N(12)-Mn(3)-O(7)	82.50(19)
O(2)-Mn(2)-N(6)	85.7(3)	N(2)#1-Mn(3)-O(7)	99.30(19)
O(6)-Mn(2)-O(5)	95.8(2)	O(9)-Mn(4)-O(3)	176.0(2)
O(2)-Mn(2)-O(5)	89.5(3)	O(9)-Mn(4)-N(11)	88.1(2)
N(6)-Mn(2)-O(5)	175.1(3)	O(3)-Mn(4)-N(11)	88.0(2)
O(6)-Mn(2)-O(8)	89.6(2)	O(9)-Mn(4)-N(7)	95.8(2)
O(2)-Mn(2)-O(8)	95.4(2)	O(3)-Mn(4)-N(7)	88.1(3)
N(6)-Mn(2)-O(8)	90.7(3)	N(11)-Mn(4)-N(7)	164.6(3)
O(5)-Mn(2)-O(8)	88.6(2)	O(9)-Mn(4)-O(6)	91.3(2)
O(6)-Mn(2)-O(1)	73.5(2)	O(3)-Mn(4)-O(6)	89.9(2)
O(2)-Mn(2)-O(1)	101.9(2)	N(11)-Mn(4)-O(6)	114.1(2)

N(6)-Mn(2)-O(1)	93.8(2)	N(7)-Mn(4)-O(6)	80.8(2)
O(5)-Mn(2)-O(1)	88.2(2)	O(9)-Mn(4)-N(9)	89.3(2)
O(8)-Mn(2)-O(1)	162.4(2)	O(3)-Mn(4)-N(9)	91.6(2)
O(6)-Mn(2)-Mn(1)	37.28(15)	N(11)-Mn(4)-N(9)	96.4(3)
O(2)-Mn(2)-Mn(1)	140.1(2)	N(7)-Mn(4)-N(9)	68.8(2)
N(6)-Mn(2)-Mn(1)	104.6(2)	O(6)-Mn(4)-N(9)	149.5(2)

Symmetry transformations used to generate equivalent atoms: #1 -x,y,-z+3/2

Table S3. BVS calculations for all manganese ions in complex **1**.

Atoms	Mn^{II}	Mn^{III}	Mn^{IV}
Mn(1)	3.518	**3.242**	3.187
Mn(2)	3.384	**3.218**	3.158
Mn(3)	**2.000**	1.846	1.813
Mn(4)	3.512	**3.243**	3.178