Mn(III)–Salen Complexes with Metallophilic Interactions

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Table S1
Crystal data and details of structure determination of complexes **1a-1c**

Compound	**1a**	**1b**	**1c**
Formula	$C_{30}H_{32}N_6O_2Mn_1Ag_1$	$C_{27}H_{26}N_4O_5Mn_1Ag_1$	$C_{18}H_{12}N_4O_2Cl_2Mn_1Ag_1$
Formula weight	671.43	649.33	550.03
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	C2/c	Cc
Cell parameters			
a /Å	11.9239(7)	22.9665(4)	11.9580(6)
b /Å	11.9781(8)	16.8217(4)	17.1565(5)
c /Å	12.3813(5)	18.4274(4)	10.9641(5)
α /°	114.351(5)	90	90.00
β /°	92.934(4)	132.066(2)	116.146(6)
γ /°	115.864(7)	90	90.00
V /Å^3	1390.9(16)	5285.1(3)	2019.20(18)
Z	2	8	4
T /K	150.0(2)	150.0(2)	150.0(2)
Density, D_c /g cm^{-3}	1.603	1.632	1.809
Abs. coefficient /mm	1.197	1.264	1.881
F(000)	684	2624	1080
Data/restraints/param.	4881/0/379	4640/3/359	2546/2/254
R_1[a] , wR_2[b] (all data)	0.1007/0.2124	0.0548/0.1283	0.0238/0.0473
R_1[a] , wR_2[b] [I > 2σ(I)]	0.0742/0.2029	0.0420/0.1232	0.0209/0.0466
Goodness of fit	1.008	1.081	0.986
CSD number	2280645	2280646	2280648

[a] $R_1 = \sum (|F_o| - |F_c|)/\sum|F_o|$.
[b] $wR^2 = \{\sum[w(F^2_o - F^2_c)^2]/\sum[w(F^2_o)^2]\}^{1/2}$

Table S2
Crystal data and details of structure determination of complexes **2a** and **2b**

Compound	**2a**	**2b**
Formula	$C_{30}H_{32}N_6O_2Mn_1Au_1$	$C_{22}H_{24}N_4O_5Mn_1Au_1$
Formula weight	760.52	676.364
Crystal system	monoclinic	triclinic
Space group	I 2/a	$P\bar{1}$
Cell parameters		
a /Å	12.6088(3)	12.1625(3)
b /Å	11.9439(2)	13.8886(5)
c /Å	19.0469(4)	15.3678(5)
α /°	90.00	94.305(3)
β /°	94.951(2)	106.002(3)
γ /°	90.00	110.229(3)
V /Å^3	2857.73(10)	2299.27(15)
Z	4	2
T /K	294(2)	150.0(2)
Density, D_c /g cm^{-3}	1.768	1.954
Abs. coefficient /mm	13.418	6.964
F(000)	1496	1312
Data/restraints/param	2611/13/180	15796/13/659
R_1[a] , wR_2[b] (all data)	0.0460/0.1283	0.0390/0.0524
R_1[a] , wR_2[b] [I > 2σ(I)]	0.0433/0.1260	0.0244/0.0502
Goodness of fit	1.122	0.9022
CSD number	2280644	2280647

[a] $R_1 = \sum (|F_o| - |F_c|)/\sum|F_o|$.
[b] $wR^2 = \{\sum[w(F^2_o - F^2_c)^2]/\sum[w(F^2_o)^2]\}^{1/2}$

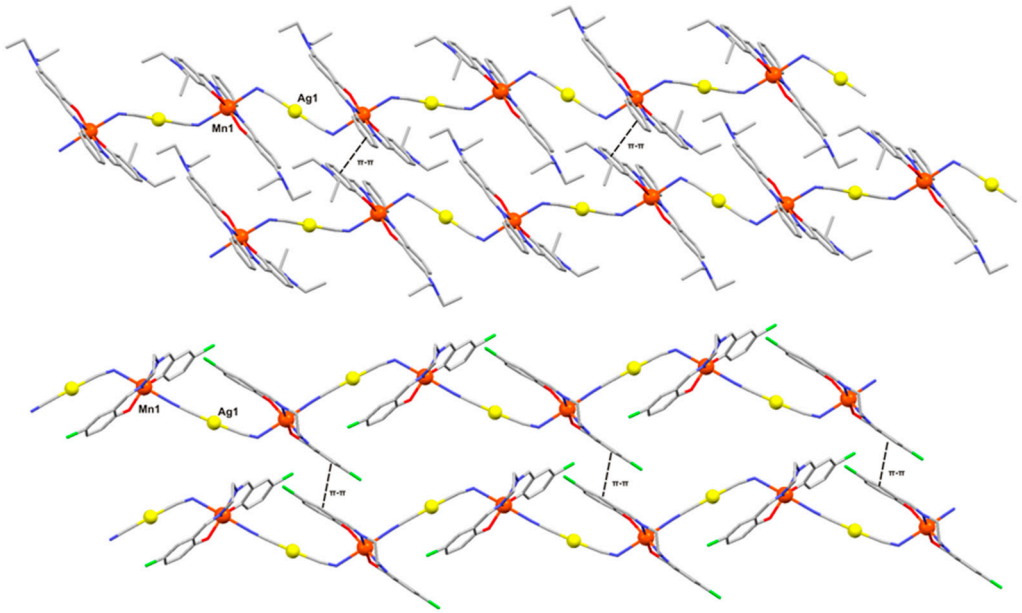


Figure S1 Projection along the *c*-axis for the complex **1a** (above) and complex **1c** (below), showing a 2D network structure, in which are shown π-π interaction between two 1D polymeric networks. The hydrogen atoms are omitted for clarity.

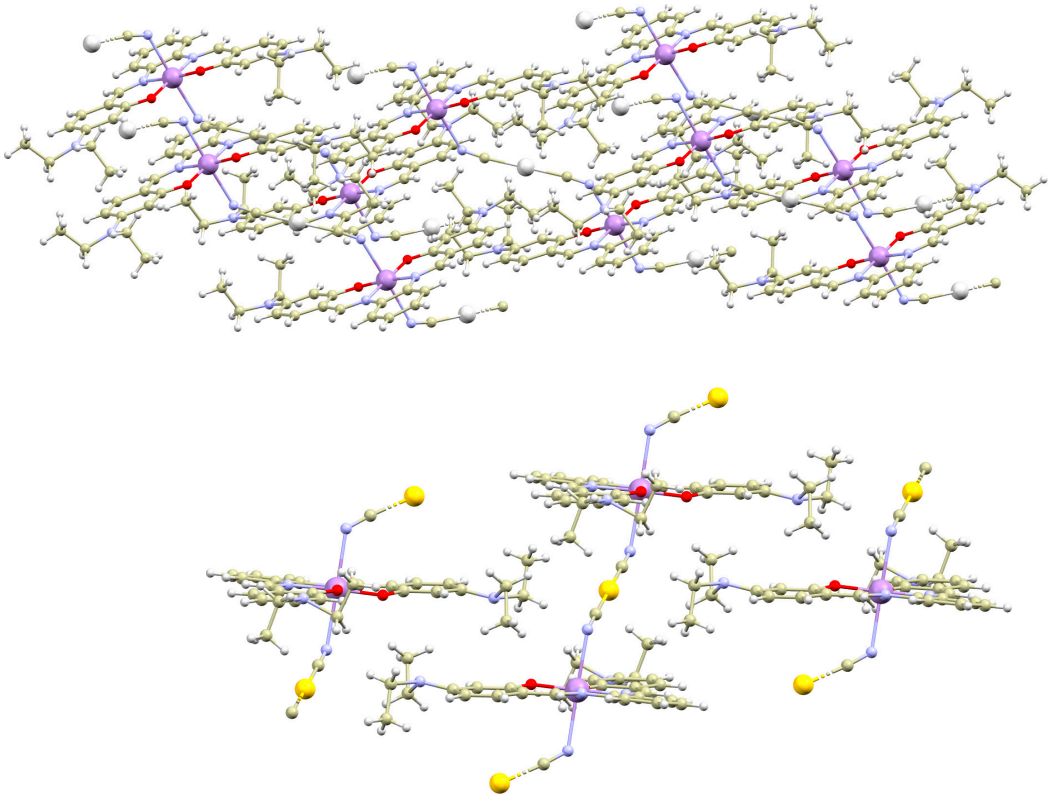


Figure S2 A perspective view illustrating localization of the Ag/Au atoms in **1a** (above) and **2a** (below).

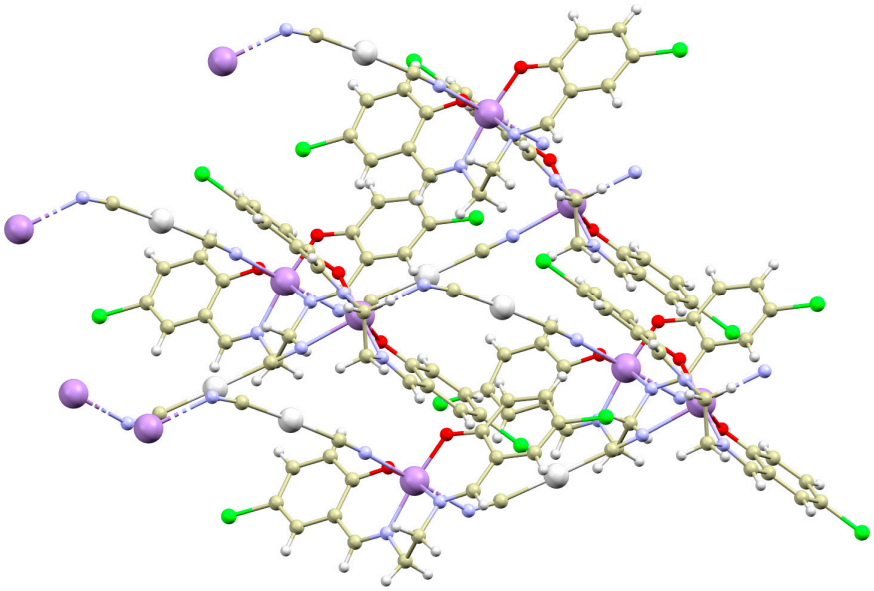


Figure S3 A perspective view illustrating localization of the Ag atoms in **1c**

Table S3 Topological and energetic properties of $\rho(\mathbf{r})$ calculated for interactions involving Ag/Au atoms. All the values are listed, having a.u. units, except for E_{int} (kcal/mol).

Compound	type	BCP	G(**r**)	V(**r**)	E_{int}	-V(**r**)/G(**r**)	h_e(**r**)	$\nabla^2\rho$(**r**)
1b	Ag···C	(3,-1)	0.00566	–0.00469	1.47	0.83	0.0009695	0.026511
2b	Au···Au	(3,-1)	0.00901	–0.00833	2.61	0.92	0.0006856	0.038795
DOKDOY	Au···Au	(3,-1)	0.00762	–0.00705	2.21	0.93	0.0005706	0.032753
GIMGAL	Ag···Ag	(3,-1)	0.01267	–0.01382	4.34	1.09	–0.001155	0.046059
TIJDOG	Ag···Ag	(3,-1)	0.01248	–0.01361	4.27	1.09	–0.001126	0.045419
TIJDUM	Au···Au	(3,-1)	0.01601	–0.01666	5.23	1.04	–0.000657	0.061392
WUJGIR	Ag···O	(3,-1)	0.00573	–0.00514	1.61	0.90	0.000589	0.025281
		(3,-1)	0.00392	–0.00327	1.03	0.83	0.000643	0.018246

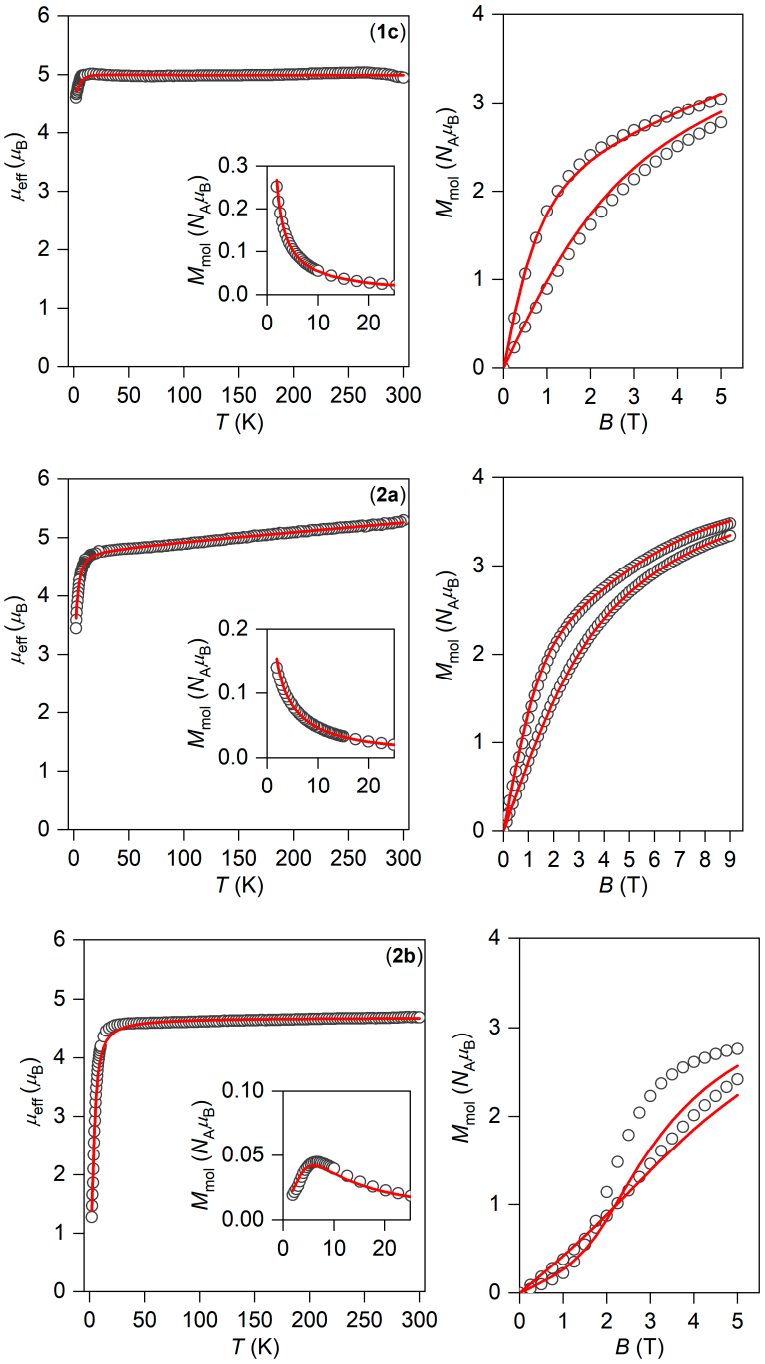


Figure S4 Temperature dependence of the effective magnetic moment and the molar magnetization (inset), and the isothermal magnetizations measured at $T = 2$ and 5 K for **1c**, **2a,** and **2b**. Empty circles – experimental data, full lines – calculated data with parameters in the text. All data are scaled per one Mn(III) ion.

Table S4 The results of BS-DFT calculations for **1a-2b**.

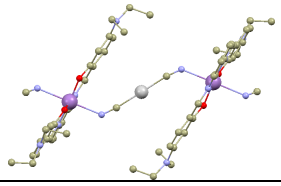
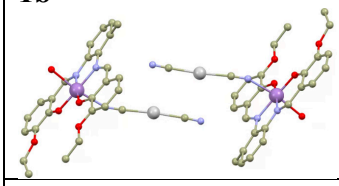
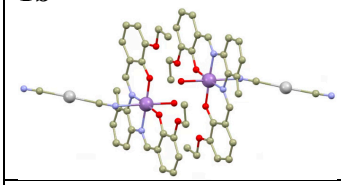
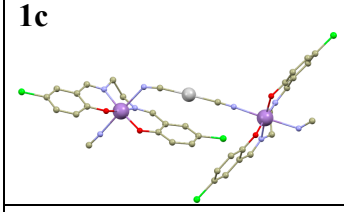
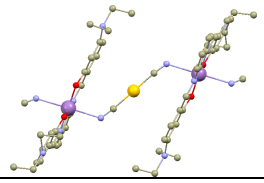
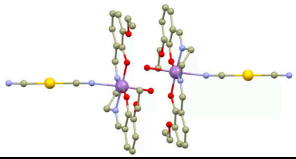
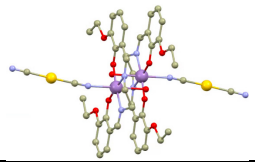
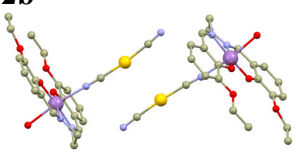
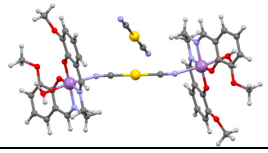
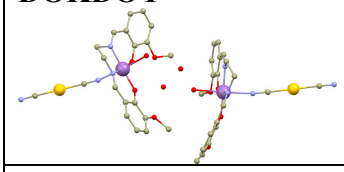
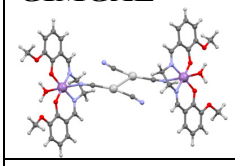
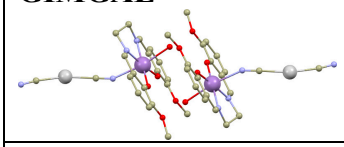
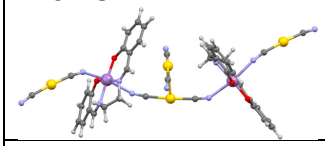
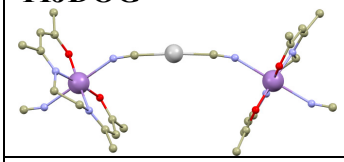
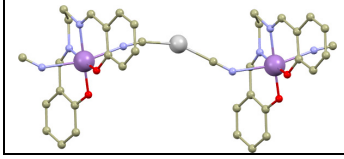
fragment	Spin Hamiltonian $-2J\times S_A\times S_B$		
	J/cm^{-1} calculated using:		
	$-(E_{HS}-E_{BS})/S_{max}$	$-(E_{HS}-E_{BS})/(S_{max}\times(S_{max}+1))$	$-(E_{HS}-E_{BS})/(S_{HS}^2-S_{BS}^2+1)$
1a 	0.0	0.0	0.0
1b 	0.0	0.0	0.0
1b 	–0.46	–0.37	–0.46
1c 	0.0	0.0	0.0
2a 	0.0	0.0	0.0
2b 	–0.60	–0.48	–0.60
2b 	–0.56	0.44	–0.56
2b 	0.0	0.0	0.0

Table S5 The results of BS-DFT calculations for Mn(III) salen-based complexes with $[Ag/Au(CN)_2]^-$ bridging complexes.

	Spin Hamiltonian $-2J \times S_A \times S_B$		
fragment	J/cm^{-1} calculated using:		
	$-(E_{HS}-E_{BS})/S_{max}$	$-(E_{HS}-E_{BS})/(S_{max}\times(S_{max}+1))$	$-(E_{HS}-E_{BS})/(S_{HS}^2 - S_{BS}^2+1)$
DOKDOY 	0.0	0.0	0.0
DOKDOY 	0.0	0.0	0.0
GIMGAL 	0.0	0.0	0.0
GIMGAL 	–0.59	–0.47	–0.59
TIJDUM 	0.0	0.0	0.0
TIJDOG 	0.0	0.0	0.0
WUJGIR 	0.0	0.0	0.0