Electronic Supplementary Information (ESI)

Structural and magnetic characterizations of the first manganese(III) Schiff base complexes involving hexathiocyanidoplatinate(IV) bridges

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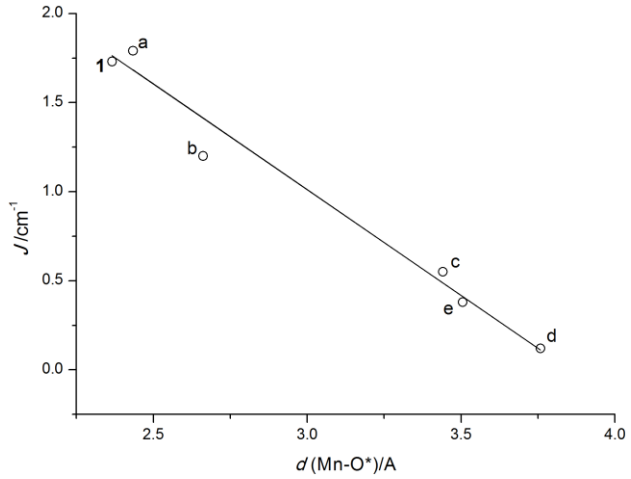

Compound	Mn-O*
a	2.434
b	2.662
c	3.441
d	3.758
e	3.505
1	2.366

Fig. S1. The correlation between the ferromagnetic exchange (J) and Mn-O* distance. The linear curve was calculated according to ref. [23]. List of compounds: [Mn(saltmen)(H_2O)]ClO_4 (a), [Mn(naphtmen)(H_2O)]ClO_4 (b), [Mn(saltmen)(NCS)] (c), [Mn(naphtmen)(NCS)] (d), [Mn(naphtmen)(Cl)] (e), [{Mn(L4a)}$_2${μ-Pt(SCN)$_6$}]$_n$ (**1**).

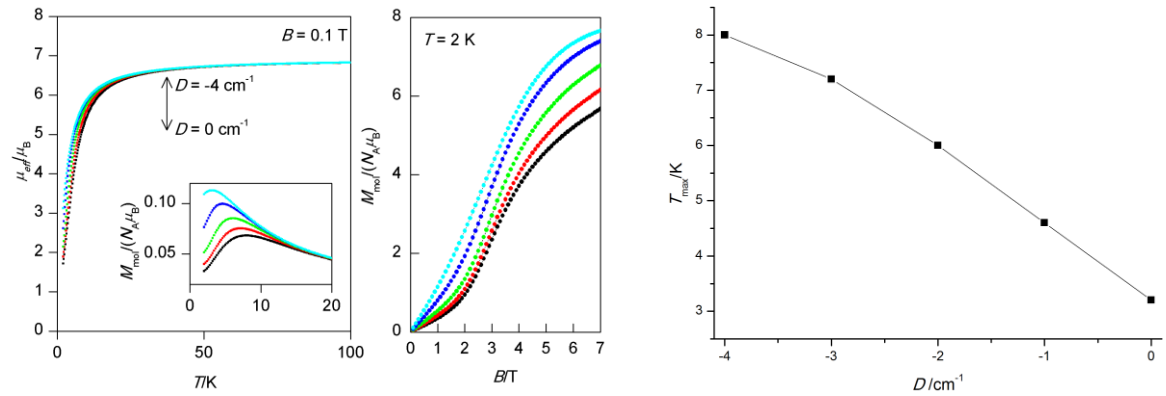

Fig. S2. *Left*: the variation of magnetic properties for $S_1 = S_2 = 2$ dimer, with the fixed parameters J = -1 cm^{-1}and g = 2.0, while D varies from -4 to 0 cm^{-1} with the step equals 1 cm^{-1}. *Right*: the effect of ZFS on the temperature corresponding to the maximum of magnetization (susceptibility).

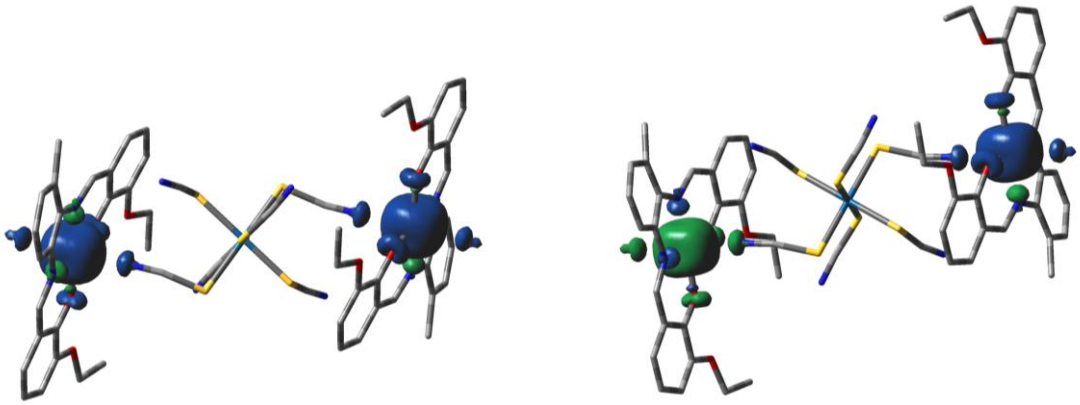

Fig. S3. The calculated spin density distribution using B3LYP/TZVP for [{Mn(L4b)(H_2O)}$_2${μ-Pt(SCN)$_6$}] (**2**). Positive and negative spin densities are represented by dark blue, and green surfaces, respectively. *Left*: the isodensity surface of high-spin (HS) state with the cutoff values of 0.005 e·boh^{-3}. *Right*: the isodensity surface of broken symmetry spin (BS) state with the cutoff values of 0.005 e·boh^{-3}.

Table S1. The DFT calculated net Mulliken spin densities (ρ), the expectation values $<S^2>$ and exchange energy (J) from HS and BS states for the supramolecular dimers [{Mn(L4a)NCS}$_2$] and [{Mn(L4b)(H$_2$O)(NCS)}$_2$] extracted from X-ray structures of **1**, and **2**, respectively.

[{Mn(L4a)NCS}$_2$] of **1**[a]			[{Mn(L4b)(H$_2$O)(NCS)}$_2$] of **2**[b]		
	HS	BS		HS	BS
ρ(Mn)	3.88	-3.88	ρ(Mn')	3.89	-3.89
ρ(N1)	-0.07	0.07	ρ(N1')	-0.07	0.07
ρ(N2)	-0.08	0.09	ρ(N2')	-0.06	0.06
ρ(N5)	0.04	-0.04	ρ(N3')	0.04	-0.04
ρ(O1)	0.02	-0.02	ρ(O1')	0.02	-0.02
ρ(O2)	0.04	-0.004	ρ(O2')	0.02	-0.02
ρ(O2')	0.04	0.004	ρ(O3')	0.03	-0.03
ρ(O1')	0.02	0.02	ρ(H1')	0.002	0.000
ρ(N5')	0.04	0.04	ρ(H2')	0.002	0.000
ρ(N2')	-0.08	-0.09	ρ(H2)	0.002	0.000
ρ(N1')	-0.07	-0.07	ρ(H1)	0.002	0.000
ρ(Mn')	3.88	3.88	ρ(O3)	0.03	0.03
			ρ(O2)	0.02	0.02
			ρ(O1)	0.02	0.02
			ρ(N3)	0.04	0.04
			ρ(N2)	-0.06	-0.06
			ρ(N1)	-0.07	-0.07
			ρ(Mn)	3.89	3.89
$<S^2>$	20.08	4.08	$<S^2>$	20.09	4.09
$J_{Mn\text{-}OPh\text{-}Mn}$ = +1.74 cm^{-1}			$J_{Mn\text{-}Owater\text{-}H...OPh\text{-}Mn}$ = -0.45 cm^{-1}		

[a] Symmetry code for atoms with the apostrophe: 1-x, 1-y, 1-z. [b] Symmetry code for atoms with the apostrophe: 1-x, -y, 1-z; HS = high-spin state, BS = broken-symmetry spin state.

Table S2. The DFT calculated net Mulliken spin densities (ρ), the expectation values $<S^2>$ and exchange energy (J) from HS and BS states of the trinuclear [{Mn(L4b)(H_2O)}$_2${μ-Pt(SCN)$_6$}] (**2**) based on a geometry following from X-ray structural determination.[a]

	HS	BS
ρ(Mn')	3.90	-3.90
ρ(N1')	-0.06	0.06
ρ(N2')	-0.06	0.06
ρ(O1')	0.02	-0.03
ρ(O2')	0.03	-0.03
ρ(O3')	0.02	-0.02
ρ(N3')	0.03	-0.03
ρ(C25')	-0.003	0.004
ρ(S1A')	0.005	-0.006
ρ(Pt)	-0.0003	0.0001
ρ(S1A)	0.005	0.006
ρ(C25)	-0.003	-0.003
ρ(N3)	0.03	0.03
ρ(O3)	0.02	0.02
ρ(O2)	0.03	0.03
ρ(O1)	0.02	0.02
ρ(N2)	-0.06	-0.06
ρ(N1)	-0.06	-0.06
ρ(Mn)	3.90	3.90
$<S^2>$	20.07	4.07
J = -0.027 cm^{-1}		

[a] Symmetry code for atoms with the apostrophe: -x, -y, -z