Supplementary Material (ESI) for Chemical Communications

Preparation, Structure, and Magnetic Interaction of a $Mn(hfac)_2$-bridged [2-(3-Pyridyl)(Nitrony Nitroxide)-$Mn(hfac)_2]_2$ Chain Complex

Keiji Okada,*[a] Shiori Beppu,[a] Koichiro Tanaka,[a] Masato Kuratsu,[a] Kimiaki Furuichi,[a] Masatoshi Kozaki,[a] Shuichi Suzuki,[a] Daisuke Shiomi,*[a] Kazunobu Sato,[a] Takeji Takui,[a] Yasutaka Kitagawa,[b] and Kizashi Yamaguchi*[b]

Supplementary Information

1. Synthesis of $\mathbf{1}_2$·$[Mn(hfac)_2]_3$

A pressure-equalizing dropping funnel type drying tube containing molecular sieve (4 Å, 5 g) was inserted between a round bottom flask and a reflux condenser fitted with a drying tube ($CaCl_2$). A suspension of commercial $Mn(hfac)_2$ (116 mg) containing a small amount coordinating water in dry heptane (25 ml) in the round bottom flask was refluxed for 5 h, during which the suspension became a yellow solution. After cooling the reaction mixture to room temperature, compound **1** (38.5 mg) in dry methylene chloride (5 ml) was added to the heptane solution of $Mn(hfac)_2$. After standing overnight, the insoluble materials involving mainly $Mn(hafc)_2$ were removed by filtration in a glove box. Then, the filtrate was evaporated under reduced pressure in the glove box, to a give blue-green powder. The powder was recrystallized from chloroform-heptane to yield pure $\mathbf{1}_2$·$[Mn(hfac)_2]_3$ as dark green crystals (69 mg, 45% yield). mp 187 °C, IR (KBr) ν_{max}/cm^{-1} 1651, 1607,1556, 1531, 1497, 1481, 1400, 1371,1329, 1256, 1207, 1146, 1097, 800, 665, 584. Anal. Found: C, 34.47; H, 1.95; N, 4.45. Calc. for $C_{54}H_{38}F_{36}Mn_3N_6O_{16}$: C, 34.58; H, 2.04; N, 4.48%. EPR (powder) g = 2.0081 as a broad and structureless signal with a width of ca. 450 G at half height.

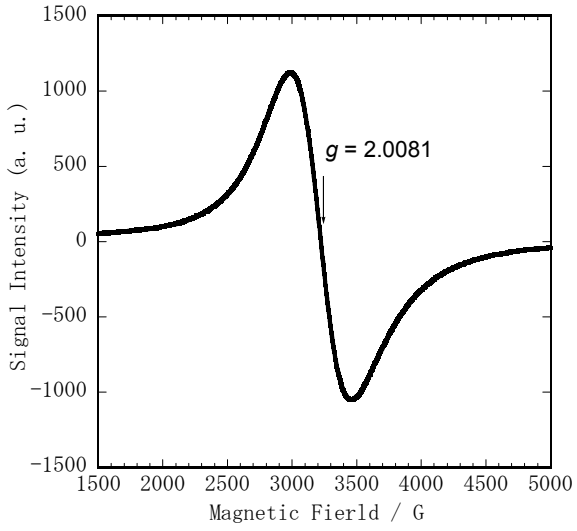


Fig. S1. The EPR spectrum of $\mathbf{1}_2$·$[Mn(hfac)_2]_3$ in a powder form measured at 123 K.

2. Table S1. Selected bond-lengths around the spin-centers of 1_2·[Mn(hfac)$_2$]$_3$.

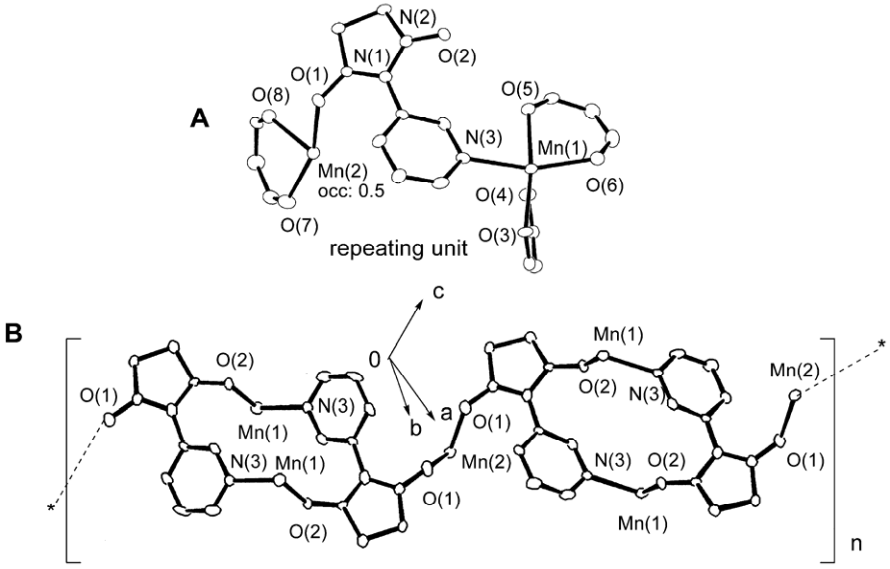
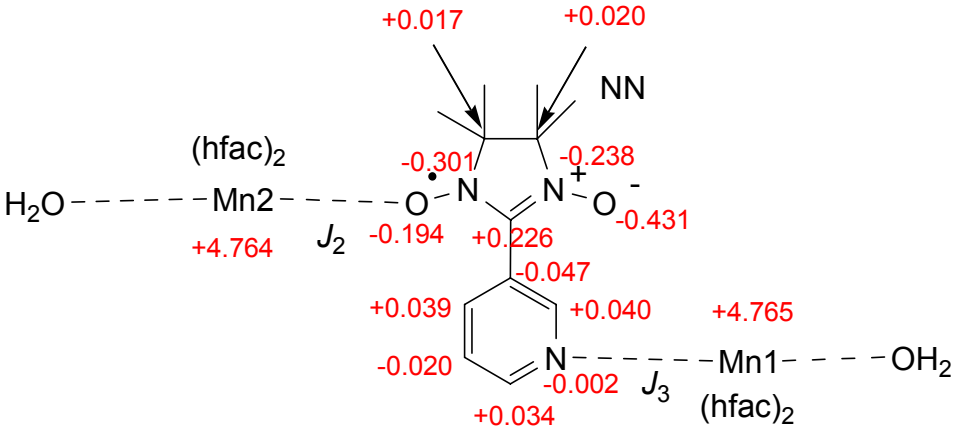


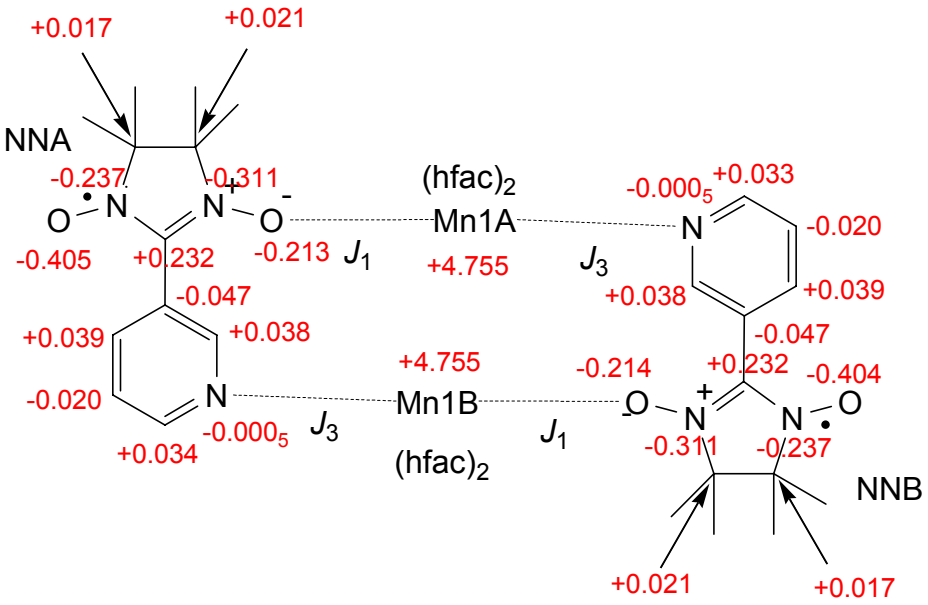
Table S1. Selected bond-lengths (Å) around the spin centers of 1_2·[Mn(hfac)$_2$]$_3$

bond	1_2·[Mn(hfac)$_2$]$_3$
Mn(1)-O(2)	2.148(4)
Mn(1)-O(3)	2.131(5)
Mn(1)-O(4)	2.154(4)
Mn(1)-O(5)	2.152(5)
Mn(1)-O(6)	2.178(3)
Mn(1)-N(3)	2.250(4)
Mn(2)-O(1)	2.138(4)
Mn(2)-O(7)	2.151(4)
Mn(2)-O(8)	2.154(4)
N(1)-O(1)	1.295(6)
N(2)-O(2)	1.306(5)

3. The atomic spin densities of the ground states of Model I and Model II



Atomic spin densities (red) for the ground state of Model I (*udu* state)



Atomic spin densities (red) for the ground state of Model II (*udud* state)