Manganese(II) octacyanotungstate(V)-based magnet containing a noncoordinated aromatic molecule

Toshinori Kashiwagi,† Shin-ichi Ohkoshi,*,†, ‡ Hidetake Seino, § Yasushi Mizobe, §
and Kazuhito Hashimoto*,†

† Research Center for Advanced Science and Technology, The University of Tokyo,
4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan
‡ PRESTO, JST, 4-1-8 Honcho Kawaguchi, Saitama, Japan
§ Institute of Industrial Science, The University of Tokyo,
4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan
e-mail: ohkoshi@light.t.u-tokyo.ac.jp, hashimoto@light.t.u-tokyo.ac.jp
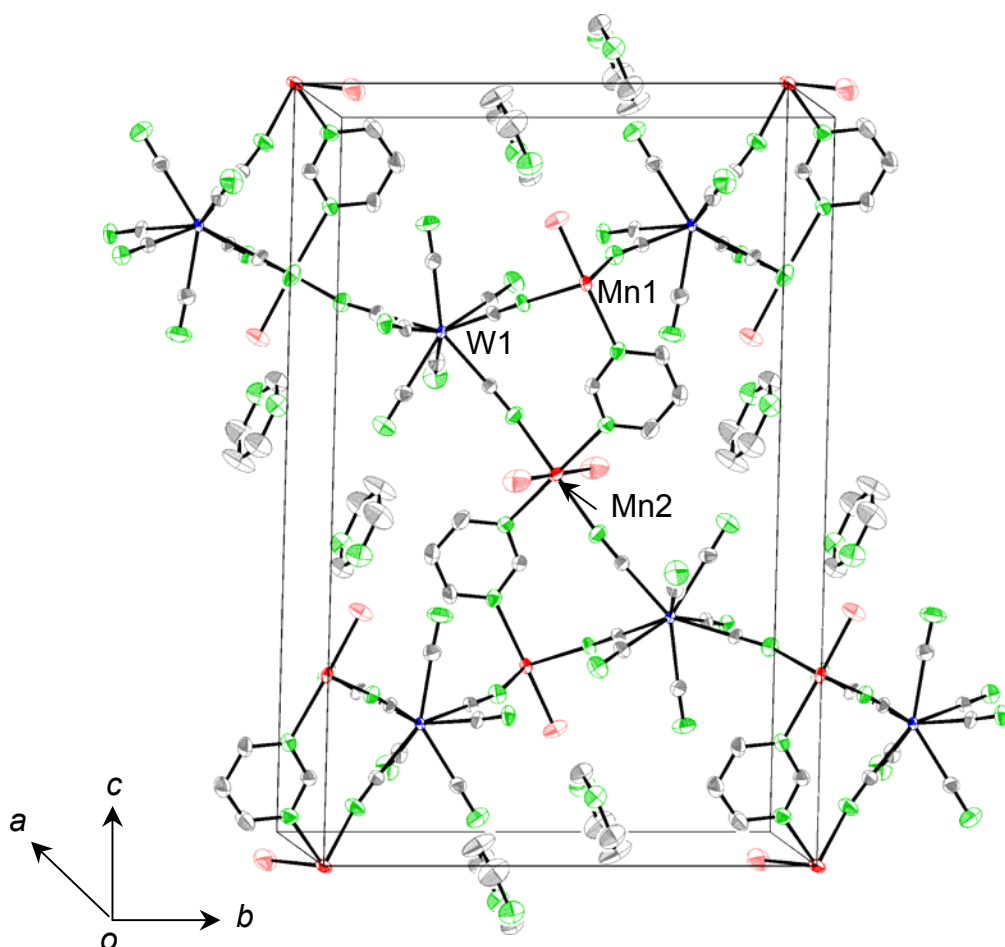
SUPPORTING INFORMATION

Figure S1.   A view of the unit cell of [{Mn^{II}(pyrimidine)(H$_2$O)}$_2${Mn^{II}(H$_2$O)$_2$}-{W^V(CN)$_8$}$_2$](pyrimidine)$_2$·2H$_2$O.
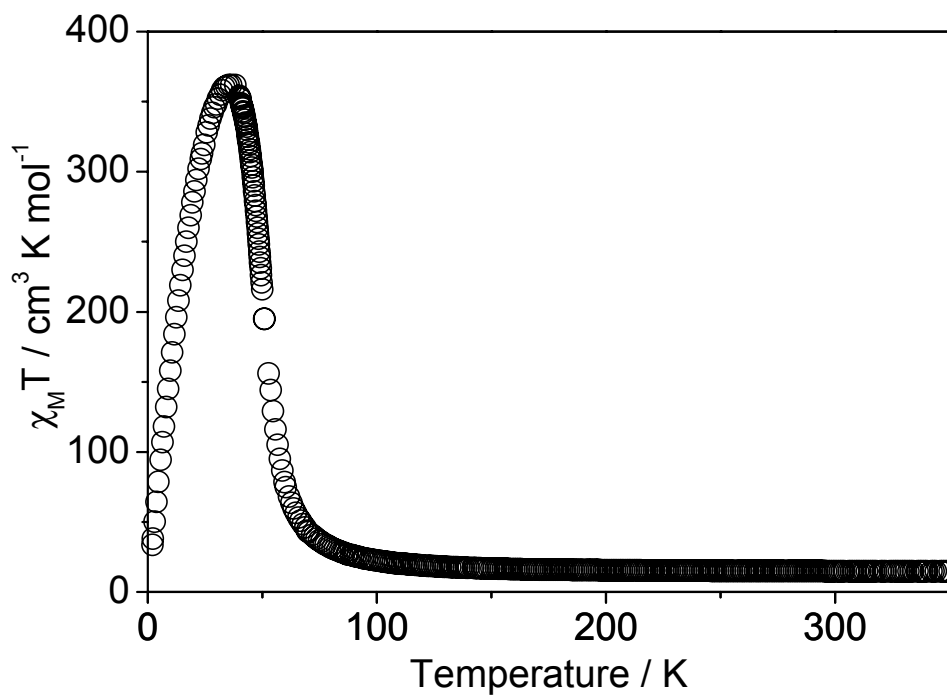
Figure S2. Temperature dependence of $\chi_M T$ value of [{Mn^{II}(pyrimidine)(H$_2$O)}$_2$-{Mn^{II}(H$_2$O)$_2$}{W^V(CN)$_8$}$_2$](pyrimidine)$_2$·2H$_2$O.
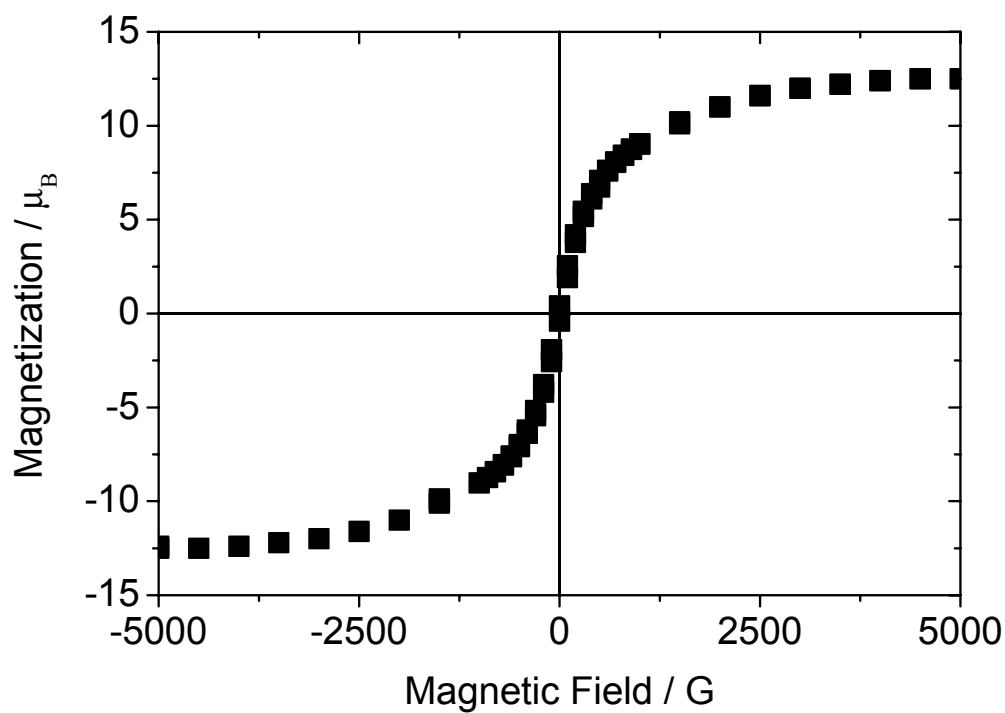
Figure S3. The magnetic hysteresis loop of [{Mn^{II}(pyrimidine)(H$_2$O)}$_2${Mn^{II}(H$_2$O)$_2$}-{W^V(CN)$_8$}$_2$](pyrimidine)$_2$·2H$_2$O.

(a)

(b)

d_{z^2} (W1) $d_{x'y'}$ (Mn1)

(c)
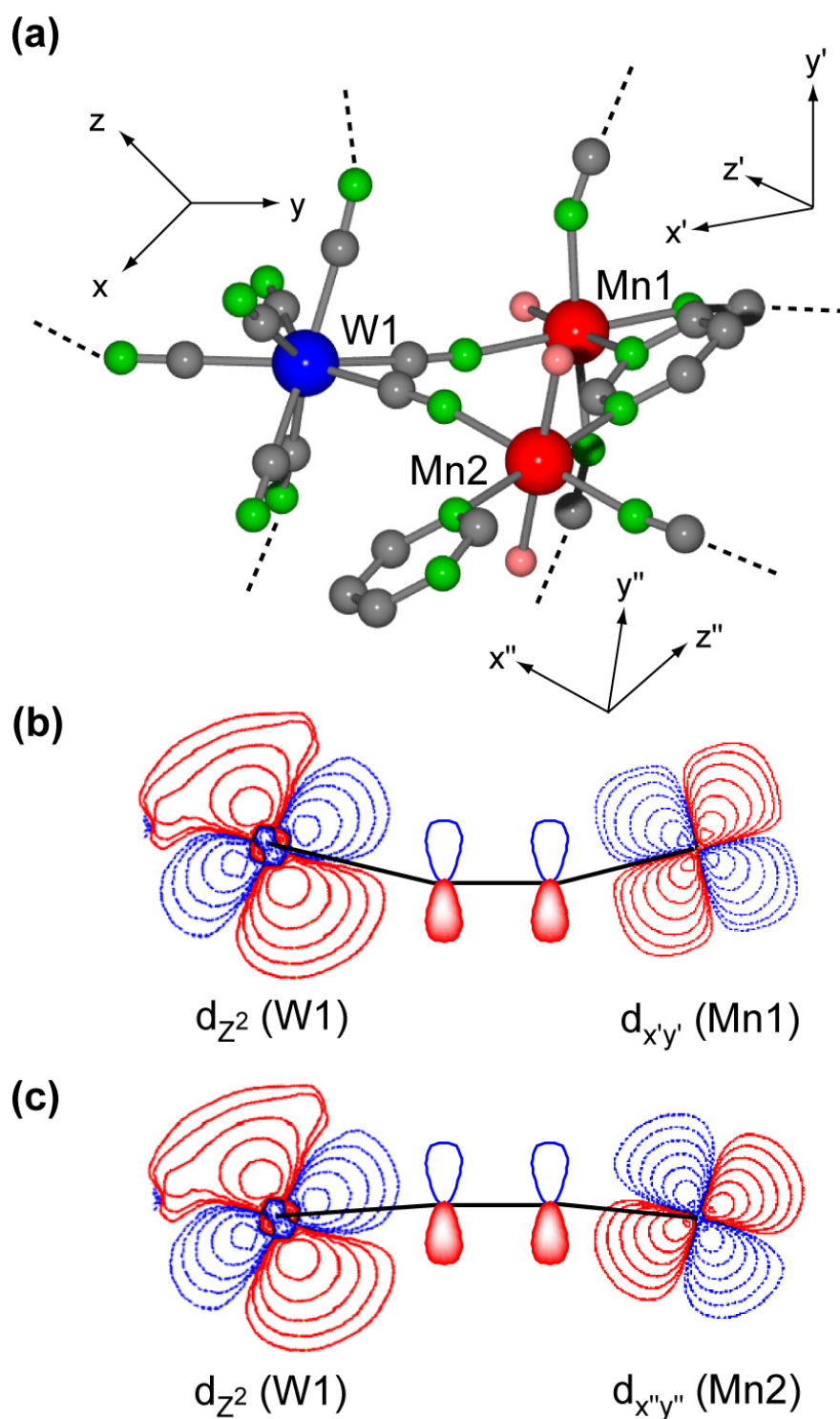
d_{z^2} (W1) $d_{x''y''}$ (Mn2)

Figure S4. **Schematic illustration of the superexchange pathways between W^V and Mn^{II} (Mn1 and Mn2) site through the bridged cyanide. (a) The geometric structures and molecular symmetric axes. (b) The magnetic orbitals on $W(CN)_8$ and $Mn1(CN)_4(H_2O)(pyrimidine)$ units. (c) The magnetic orbitals on $W(CN)_8$ and $Mn2(CN)_2(H_2O)_2(pyrimidine)_2$ units.**

The coordination geometries of the W and Mn sites are C_{2v} and D_{4h}, respectively (Figure S4a). DV-Xα calculation for the W and Mn units suggests that one 5d orbital (A_1) of W and five 3d orbitals (B_{1g}, B_{2g}, A_{2g}, and two A_{1g}) of Mn1 are magnetic orbitals. Considering the directions of magnetic orbitals and the molecular symmetrical axes of the W and Mn1 sites, the antiferromagnetic superexchange interaction in the grid layer is expected to operate between the A_1 (d_{z^2}) orbital of W and the A_{2g} ($d_{x'y'}$) orbital of Mn1 through the orbitals of a CN group (Figure S4b). A magnetic interaction between the A_1 (d_{z^2}) orbital of W and the A_{2g} ($d_{x''y''}$) orbital of Mn2 through the cyano-bridge is also expected to be antiferromagnetic (Figure S4c). Hence, this compound shows ferrimagnetism and T_C value of 47 K is higher than that of $Cs^I[\{Mn^{II}(3\text{-cyanopyridine})_2\{W^V(CN)_8\}\}]\cdot H_2O$ (T_C= 35 K) because the magnetic interaction between layers through the Mn2 pillar complex is added. As for the magnetic coupling between Mn1 and Mn2 through coordinated pyrimidine molecule, its coupling constant is considered to be very small because the distance through bonds is too long, i.e., d(Mn1-N9-C9-N10-Mn2) = 7.31 Å.