Electronic Supporting Information (ESI)

Unlocking single molecule magnetism: a supramolecular strategy for isolating neutral Mn^{III} salen-type dimer in crystalline environments

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Table of Contens

§1. Experimental Section

General procedures and materials

All chemicals and solvents used during the synthesis were of reagent grade. The H_2-MeOsalen (4.5651g, 92.7% yield) was synthesized by mixing ethylenediamine (0.9015 g, 15.0 mmol) with 2-Hydroxy-5-methoxybenzaldehyde (4.5645 g, 30.0 mmol) in methanol at room temperature. Elemental analyses were carried out by using a CHN analyzer (CE440, Exeter Analytical, Inc.) at the Instrumental Analysis Division, Equipped Management Center, Creative Research Institution, Hokkaido University.

Synthesis

Preparation of [Mn(5-MeOsalen)(H$_2$O)]PF$_6$

The manganese complex was prepared by mixing manganese(III) acetate dihydrate, H_2-MeOsalen and NH_4PF_6 in MeOH in a molar ratio of 1:1:1 according to the method reported previously.[S1]

Preparation of (DB24C8)[Mn(5-MeOsalen)Cl](**1**)

The appropriate hydrochloride salt and [Mn(5-MeOsalen)(H$_2$O)]PF$_6$ were mixed, and the neutral ligand H_2O was replaced with the anionic ligand Cl. At room temperature an acetone solution (30 mL) of DB24C8 (1.615 g, 3.6 mmol) was added to a methanol solution (4 mL) of [Mn(5-MeOsalen)Cl] (425.1 mg, 0.95 mmol) to form a layer. The product was then allowed to stand for one week at room temperature in the dark to form black block crystals (554.8 mg, 72.5 % yield). The resulting crystals were washed with acetone and dried under a vacuum at 50°C.

Anal. Calced for $C_{60}H_{68}N_4O_{16}Cl_2Mn_2$: C, 56.21; H, 5.35; N, 4.37. Found: C, 56.22; H, 5.34; N, 4.32.

Analysis

Crystal structure analysis

  Single-crystal X-ray diffraction (XRD) measurements of all compounds were performed using a RIGAKU MicroMax-007HF diffractometer equipped with a Cu Kα (λ = 1.54184 Å) X-ray radiation source and a Pilatus 200 K detector. A single crystal was mounted on a CryoLoop (Hampton Research) using Paratone® 8277 (Hampton Research). Data collection, cell refinement, and data reduction were performed using CrysalisPRO (Rigaku Oxford Diffraction 2017). The structures were determined using direct methods with SHELXT[S2] and refined using full-matrix least-squares techniques on F^2 with SHELX [S3] compiled in the OLEX2 package.[S4] Crystal anisotropic thermal parameters were assigned to all non-hydrogen atoms. The CCDC deposition number was 2329659.

PXRD patterns were measured using a Rigaku RINT2100 equipped with a CuKα (λ = 1.5418 Å) X-ray radiation source in the 2θ range of 5-40° at a scanning rate of 1.2 K min^{-1} (Fig. S3).

<u>Stabilization energy calculation</u>

The intermolecular interactions between [Mn(5-MeOsalen)Cl] and DB24C8 were estimated from single-point computations at the B3LYP/6-31G(d,p) level.[S5,S6] Grimme's D3 dispersion model was used for dispersion correction.[S7] Computations were performed using the GAUSSIAN16 code set. To remove errors due to the overestimation of the stabilization energy (basis set superposition error), counterpoise correction implemented in GAUSSIAN16 was applied.

<u>Magnetic measurement</u>

Magnetic susceptibility was measured using a Quantum Design MPMS3 at the Faculty of Science, Hokkaido University, under 1000 Oe in a temperature range of 300 to 2 K (Fig. S4). Magnetization measurements were conducted on the same equipment at 1.8 K (Fig. S5) with a dc magnetic field ranging from −7 to 7 T. Magnetic susceptibility measurements were performed using a Quantum Design MPMS-XL at various frequencies from 1 to 1488 Hz with an ac field amplitude of 3 Oe in the temperature range of 1.8 to 2.4 K. The measurements were performed on polycrystalline samples. Experimental data were corrected by the trace background values of the sample holder and by the diamagnetic contribution calculated from Pascal constants.[S8]

§2. Single crystal X-ray analysis

Table S1. Crystallographic data and structural refinement of crystal **1**.

Crystal	**1**
Temperature / K	293
Crystal Dimensions / mm^3	0.14×0.03×0.03
Chemical formula	$C_{30}H_{34}ClMnN_2O_8$
Formula weight	640.98
Crystal system	*Triclinic*
Space group	$P\bar{1}$
a / Å	10.4886 (7)
b / Å	11.1906 (6)
c / Å	12.9544 (7)
α / deg	90.277 (4)
β / deg	102.249 (5)
γ / deg	98.094 (5)
V / Å^3	1470.14 (15)
Z	2
D_{calc} / g·cm^{-3}	1.448
μ(Cu K$_\alpha$) / cm^{-1}	4.943
$2\theta_{max}$ / *deg*	146.41
Reflections measured	15676
Independent reflections	5577
Reflections used	5577
R_1 [a]	0.0687
R_w (F^2) [a]	0.1860
GOF	0.951
CCDC No.	2329659

[a] $R_1 = \Sigma||F_o| - |F_c||$ /$\Sigma|F_o|$ and $R_w = (\Sigma\omega(|F_o| - |F_c|)^2$ /$\Sigma\omega F_o^2)^{1/2}$.
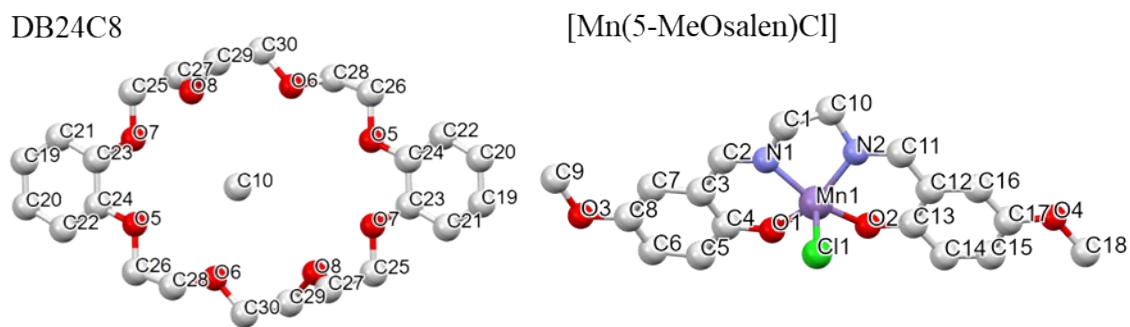
Fig. S1. Crystallographically independent structures of crystal **1** at 293 K (Note that DB24C8 is crystallographically independent in a half-structure but is represented as a single molecule for clarity.). Mn, Cl, C, N, and O atoms are depicted in purple, green, gray, blue, and red, respectively. All the molecules are depicted as ellipsoid models. Hydrogen atoms were omitted for clarity.

Table S2. Distances and angle of [Mn(5-MeOsalen)Cl] inter or intra dimer in crystal **1** at 293 K.

Atomic distance	Distance / Å	Angle / degree
Mn1•••Cl1	2.397(1)	-
Mn1•••N1	2.000(3)	-
Mn1•••N2	2.006(4)	-
Mn1•••O1	1.906(4)	-
Mn1•••O2	1.883(3)	-
Mn1•••Mn1*	4.2497(8)	-
Mn1•••O1*	3.914(3)	-
Mn1•••O1•••Mn1*	-	86.6(1)

The asterisk (*) indicates atoms outside the plane with symmetry operation; 2-x, 1-y, 1-z

Table S3. Distances and angles of C-H•••O interactions between [Mn(5-MeOsalen)Cl]•••DB24C8 in crystal **1** at 293 K.

| C-H•••O interaction	C•••O distance / Å	H•••O distance / Å	C-H•••O Angle / degree
C1•••O6	3.621(5)	2.750	149.83
C1•••O8	4.062(5)	2.471	151.85
C2•••O7	3.668(6)	2.752	168.65
C10•••O5	3.478(6)	2.624	146.94
C10•••O6	3.187(6)	2.686	112.58
C11•••O7	3.432(5)	2.749	131.03

Symmetry operation; 2-x, 1-y, 1-z

closest C•••C : 3.389 Å
phenyl ring π•••π : 5.157 Å
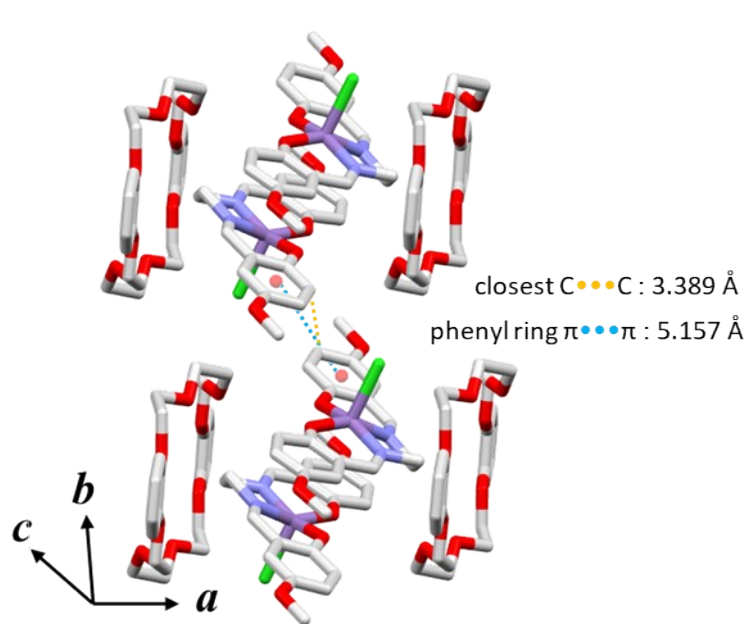
Fig. S2. Slight contact between the [Mn(5-MeOsalen)(Cl)] dimers in the *b*+*c* axis direction in crystal **1** at 293 K. Mn, Cl, C, N, and O atoms are depicted in purple, green, gray, blue, and red, respectively. All molecules are depicted as ellipsoid models. Hydrogen atoms are omitted for clarity. The distances between the closest C-C (3.389 Å)and the centers of the phenylene rings π•••π (5.157 Å) are indicated by orange and blue lines, respectively.

§3. Magnetic properties

PXRD was used to identify the purity of the products obtained prior to AC and DC magnetic susceptibility measurements.
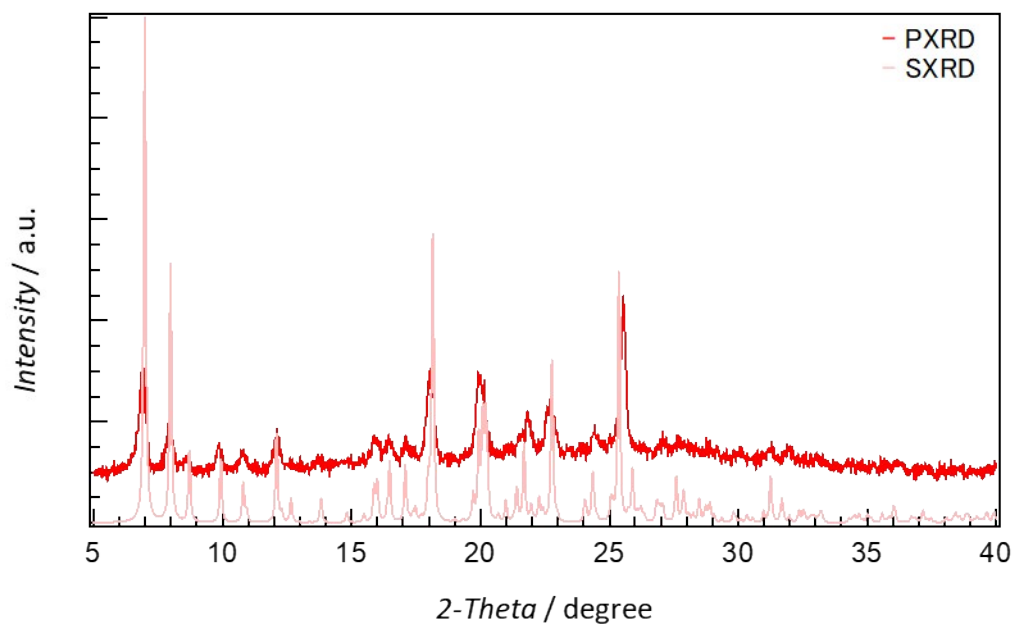
Fig. S3. The powder X-ray diffraction (PXRD) patterns of crystal **1 were** measured at room temperature. The simulated patterns were compared with the experimental patterns to confirm the purity of the samples.
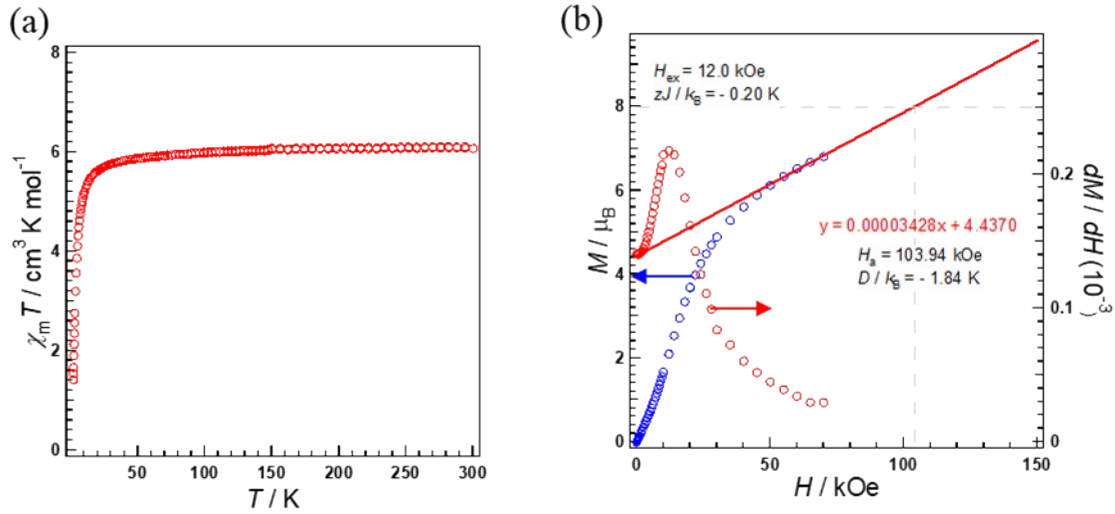
Fig. S4. (a) Temperature dependence of molar magnetic susceptibility of crystal **1** ($\chi_m T$ vs. T plot). The value of $\chi_m T$ coincides with the saturation value of 6 cm³ K mol⁻¹ for matter with an $S_T = 4$ ground state. (b) Field dependence of magnetization of crystal **1.** The dashed line represents the expected saturation of the magnetization at $M_{sat} = g S_T$ (Lande factor g = 2.0). The solid red lines are linear fits of the high-field magnetization above 50 kOe and their intersection with $M_{sat,}$ corresponding to H_a. H_{ex} is the value of the magnetic field corresponding to the maximum value of dM / dH.
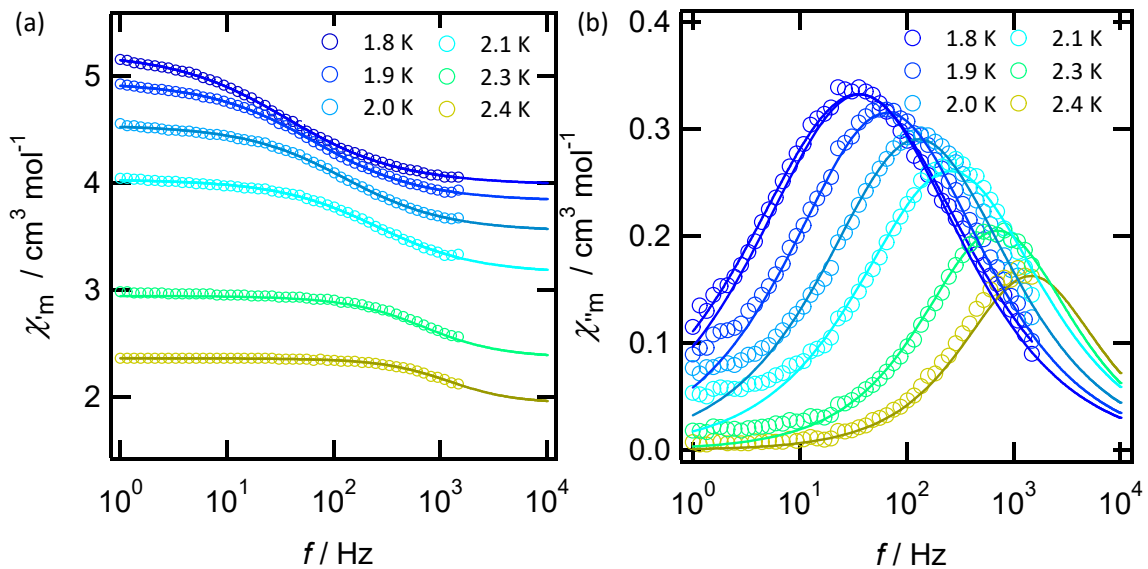
Fig. S5. Magnetic relaxation phenomena of the **1**. Frequency dependence of (a) real (χ_m') and (b) imaginary (χ_m'') parts of AC susceptibility measured at several temperatures under zero dc field and 3 Oe ac field. Measurements were made in the frequency range of 1-1488 Hz and temperature range of 1.8-2.4 K. Solid lines are theoretical curves from the fitting.

The equations used for fitting χ'_m and χ''_m are shown below:

$$\chi'_m(\omega) = \chi_s + (\chi_T - \chi_s)\frac{1 + (\omega\tau)^{1-\alpha}sin(\pi\alpha/2)}{1 + 2(\omega\tau)^{1-\alpha}sin(\pi\alpha/2) + (\omega\tau)^{2-2\alpha}} \qquad (1)$$

$$\chi''_m(\omega) = (\chi_T - \chi_s)\frac{(\omega\tau)^{1-\alpha}cos(\pi\alpha/2)}{1 + 2(\omega\tau)^{1-\alpha}sin(\pi\alpha/2) + (\omega\tau)^{2-2\alpha}} \qquad (2)$$

where χ_S and χ_T are the adiabatic and isothermal limits of susceptibility, respectively. ω is the angular frequency, and α is the distribution of relaxation times about τ. The values obtained by fitting are listed in Table S3.

Table S4 Fitting parameter for magnetic relaxation of **1**.

Temperature / K	χ_s	χ_T	τ	α
1.8	3.975(5)	5.221(5)	4.3(6)×10^{-3}	0.375(6)
1.9	3.823(6)	4.945(4)	2.43(4)×10^{-3}	0.348(6)
2.0	3.54(1)	4.541(4)	1.25(3)×10^{-3}	0.330(9)
2.1	3.15(2)	4.032(4)	6.2(3)×10^{-4}	0.32(1)
2.3	2.37(2)	2.954(2)	2.26(6)×10^{-4}	0.219(9)
2.4	1.935(3)	2.361(7)	1.1(1)×10^{-4}	0.169(6)

The temperature range of the measurement was 1.8-3.5 K, the fitting was successful only below 2.4 K, where a relaxation phenomenon were observed.

§4. References

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