## **Supplementary Information**

Anion-Controlled Assembly of Four Manganese Ions: Structural, Magnetic, and Electrochemical Properties of Tetramanganese Complexes Stabilized by Xanthene-Bridged Schiff Base Ligands

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## **Experimental**

**General Procedures.** The chemicals for the synthesis of the compounds were purchased from commercial sources and used as received. 3-Amino-1-propanol was purchased from Tokyo Chemical Industry Co., Ltd. 5,5' -(9,9-Dimethylxanthene-4,5-diyl)bis(salicylaldehyde) (H<sub>2</sub>xansal) was prepared according to a literature procedure.<sup>1</sup> NMR spectra were recorded on a Bruker AVANCE 300 FT-NMR spectrometer at room temperature. IR spectra were recorded on a JASCO FT/IR-6200 spectrometer with an attenuated total reflection (ATR) accessory. Electrospray ionization (ESI) mass spectrometer. Elemental analyses were performed by the Analytical Research Service Center at Osaka City University on J-SCIENCE LAB JM10 or FISONS Instrument EA1108 elemental analyzers.

Synthesis of H<sub>4</sub>L. To a suspension of H<sub>2</sub>xansal (0.45 g, 1.0 mmol) in ethanol (10 mL) was added a solution of 3-amino-1-propanol (0.15 g, 2.0 mmol) in ethanol (10 mL). The resulting yellow suspension was refluxed for 30 min, and then cooled to room temperature. The yellow crystalline precipitate was collected by filtration, washed with ethanol, and dried under reduced pressure. Yield: 0.48 g (85%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.73 (s, 6H, CH<sub>3</sub>), 1.4–2.1 (s, br, 2H, CH<sub>2</sub>OH), 1.98 (tt, *J* = 6.1, 6.5 Hz,

4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.63 (td, J = 6.5, 1.0 Hz, 4H, NCH<sub>2</sub>), 3.82 (t, J = 6.1 Hz, 4H, CH<sub>2</sub>OH), 6.89 (d, J = 8.5 Hz, 2H, 3-sal), 7.10–7.22 (m, 6H, 6-sal and xan-CH), 7.35–7.45 (m, 4H, 4-sal and xan-CH), 7.54 (s, br, 2H, N=CH), 13.9 (s, br, 2H, sal-OH). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  32.7, 33.2, 34.6, 54.1, 60.0, 116.9, 117.9, 123.4, 125.1, 127.4, 128.7, 128.8, 130.7, 133.3, 133.9, 147.2, 161.5, 164.9. Anal. Calcd for C<sub>35</sub>H<sub>36</sub>N<sub>2</sub>O<sub>5</sub>: C 74.45, H 6.43, N 4.96. Found: C 74.17, H 6.34, N 4.90. IR (ATR, cm<sup>-1</sup>): 3289, 3064, 2945, 2897, 2850, 1633, 1585, 1497, 1466, 1420, 1397, 1379, 1355, 1280, 1227, 1179, 1135, 1055, 876, 829, 787, 741.

Synthesis of  $[Mn_4(L)_2(\mu - OAc)_2] \cdot 1.5 CH_2 Cl_2 \cdot 0.5^i PrOH$  (1). To a vellow suspension of H<sub>4</sub>L (100 mg, 0.18 mmol) in ethanol (15 mL) was added  $Mn(CH_3COO)_2 \cdot 4H_2O$  (88 mg, 0.36 mmol). The mixture was stirred at room temperature for 1 h. The resulting dark brown suspension was refluxed for 1 h. After cooling to room temperature, the precipitate was collected by filtration, washed with ethanol, and dried under reduced pressure to afford a moss green powder (108 mg). A dichloromethane solution (100 mL) of the product was layered with 2-propanol (75 mL) and allowed to stand at room temperature for 3 days. Dark brown crystals of 1 were deposited, collected by filtration, washed with 2-propanol, and dried under reduced Yield: pressure. 51 mg (36%). Anal. Calcd for C<sub>74</sub>H<sub>70</sub>Mn<sub>4</sub>N<sub>4</sub>O<sub>14</sub>·1.5CH<sub>2</sub>Cl<sub>2</sub>·0.5'PrOH: C 57.21, H 4.80, N 3.47. Found: C 57.39, H 4.69, N 3.57. Four dichloromethane and two 2-propanol molecules of crystallization were found in the crystal structure of 1, and were partially lost on drying. IR (ATR, cm<sup>-1</sup>): 1626, 1568, 1541, 1487, 1458, 1431, 1414, 1385, 1315, 1227, 1173, 1134, 1066, 985, 877, 833, 812, 795, 748. UV-Vis:  $\lambda_{max}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm 368 ( $\varepsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 14700).

Synthesis of  $[Mn_4(L)_2Cl_3(\mu_4-Cl)(OH_2)]\cdot 6H_2O$  (2). To a yellow suspension of H<sub>4</sub>L (20 mg 0.036 mmol) in ethanol (4 mL) was added an ethanol solution (1 mL) of MnCl<sub>2</sub>·4H<sub>2</sub>O (14 mg, 0.072 mmol). The mixture was stirred at room temperature for 1 h. Triethylamine (20 µL, 0.14 mmol) in ethanol (1 mL) was added, and the mixture was stirred at room temperature for 1 h. The brown solution was evaporated and recrystallized from a methanol solution by slow diffusion of diethyl ether to give brown crystals of **2**. Yield: 19 mg (67%). Anal. Calcd for C<sub>70</sub>H<sub>66</sub>Cl<sub>4</sub>Mn<sub>4</sub>N<sub>4</sub>O<sub>11</sub>·6H<sub>2</sub>O: C 52.25, H 4.89, N 3.48. Found: C, 52.02; H, 4.92; N, 3.39. Seven water molecules of crystallization were found in the crystal structure of **2**, and were partially lost on drying. IR (ATR, cm<sup>-1</sup>): 1614, 1541, 1453, 1433, 1411, 1384, 1309, 1295, 1236, 1139, 1068,

984, 823, 795, 742. UV-Vis:  $\lambda$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm 410 (shoulder,  $\varepsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 11000).

**Magnetic Susceptibility Measurements.** The magnetic susceptibility measurements were carried out for 1 and 2 by using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS2) in the temperature range 1.7–300 K (Figure S1). The applied magnetic field was 1 T. The diamagnetic components were estimated from Pascal's constants.

The  $\chi T$  value of **1** at 300 K is 13.34 cm<sup>3</sup> K mol<sup>-1</sup>, which is slightly below the spin only value of 14.75 cm<sup>3</sup> K mol<sup>-1</sup> expected for two high-spin Mn<sup>II</sup> and two high-spin Mn<sup>III</sup> centers with g = 2.0. At lower temperature, the  $\chi T$  value decreases to 2.23 cm<sup>3</sup> K mol<sup>-1</sup> at 1.7 K. The magnetic susceptibility data of **1** was fitted by the Curie-Weiss law  $\chi = C/(T-\theta)$  with C = 13.71 cm<sup>3</sup> K mol<sup>-1</sup> and  $\theta = -8.9$  K.

The magnetic susceptibility data of **2** showed that the  $\chi T$  values decreases from 7.81 cm<sup>3</sup> K mol<sup>-1</sup> at 300 K to 0.29 cm<sup>3</sup> K mol<sup>-1</sup> at 1.7 K. The  $\chi T$  value at 300 K is much smaller than the spin only value of 12.00 cm<sup>3</sup> K mol<sup>-1</sup> expected for four high-spin Mn<sup>III</sup> ions with g = 2.0. The data of **2** were analyzed using the dimer model with a weak interaction between two alkoxo-bridged Mn<sup>III</sup><sub>2</sub> units. The Heisenberg Hamiltonian model is given by

 $H = -2J[S_{\mathrm{Mn1}} \cdot S_{\mathrm{Mn2}} + S_{\mathrm{Mn3}} \cdot S_{\mathrm{Mn4}}],$ 

where  $S_{Mn1} = S_{Mn2} = S_{Mn3} = S_{Mn4} = 2$ , and *J* is the exchange interaction between Mn1 and Mn2, or Mn3 and Mn4, bridged by two alkoxide O atoms. A theoretical expression for the molar magnetic susceptibility is derived using the Van Vleck equation, and the interaction between Mn1-Mn2 and Mn3-Mn4 units  $(T - \theta_1)$  and a paramagnetic impurity term  $(C_1/(T - \theta_2))$  are included:

 $\chi_{\rm mol} = 2 \times 2N (g^2 \mu_{\rm B}^2 / k_{\rm B}) F(X) / (T - \theta_1) + C_1 / (T - \theta_2),$ 

where

 $F(X) = (exp(18X)+5exp(14X)+14exp(8X)+30) \\ /(exp(20X)+3exp(18X)+5exp(14X)+7exp(8X)+9)$ 

$$X = -J/k_BT$$

The least-squares fitting of the experimental data with this model gives J = -24.3 K (-16.9 cm<sup>-1</sup>),  $\theta_1 = -39.9$  K,  $C_1 = 1.38$  cm<sup>3</sup> K mol<sup>-1</sup>,  $\theta_2 = -6.4$  K, and g = 1.88. The *g* value may be underestimated by the paramagnetic impurity contribution.

**Electrochemistry.** Cyclic voltammetric (CV) measurements were performed at room temperature using an ALS/CHI600A voltammetric analyzer (Bioanalytical Systems Inc.). Working, reference, and counter electrodes were a glassy carbon disk

electrode with a diameter of 3 mm (Bioanalytical Systems Inc.), a  $Ag/Ag^+$  (0.01 M  $AgNO_3$ , 1 M = 1 mol dm<sup>-3</sup>) reference electrode, and a platinum wire, respectively. Sample solutions were prepared in the concentration of  $1 \times 10^{-4}$  M for 1 and  $1 \times 10^{-3}$  M for 2, and contained 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> or Bu<sub>4</sub>NCl as a supporting electrolyte. The observed potentials were corrected using the redox potential of ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) obtained under the same conditions. The cyclic voltammograms of 1 and 2 are shown in Figures S2 and S3, respectively.

Complex **1** exhibits three redox couples at  $-1.08 (\Delta E_p = 131 \text{ mV})$ ,  $-0.24 (\Delta E_p = 63 \text{ mV})$ , and 0.17 V ( $\Delta E_p = 78 \text{ mV}$ ) ( $E_{1/2}$  vs  $E^{\circ}$ , (Fc<sup>+/0</sup>)). The cathodic peak current at -1.15 V ( $i_{pc} = 2.5 \mu \text{A}$ ) is larger by a factor of 1.6 than the anodic peak current at -0.21 V ( $i_{pa} = 1.6 \mu \text{A}$ ). Furthermore, the second reduction wave was not observed even when swept to -2.4 V (Figure S2). From these results we concluded that the reduction at -1.08 V consists of two overlapped one-electron processes for Mn<sup>III</sup><sub>2</sub>Mn<sup>II</sup><sub>2</sub>/Mn<sup>II</sup><sub>4</sub>. The two quasi-reversible couples at -0.24 and 0.17 V were assigned to Mn<sup>III</sup><sub>3</sub>Mn<sup>II</sup>/Mn<sup>III</sup><sub>2</sub>Mn<sup>II</sup><sub>2</sub> and Mn<sup>III</sup><sub>4</sub>/Mn<sup>III</sup><sub>3</sub>Mn<sup>II</sup>, respectively, because the anodic peak current at -0.21 V is similar to that of the ferrocenium/ferrocene couple obtained under the same conditions. Complex **2** shows irreversible reduction waves in the range of -1.1 to -0.3 V vs  $E^{\circ}$  (Fc<sup>+/0</sup>) in the presence of Bu<sub>4</sub>NPF<sub>6</sub> or Bu<sub>4</sub>NCl as a supporting electrolyte, which are attributable to the reduction from Mn<sup>III</sup><sub>4</sub> to Mn<sup>III</sup><sub>4</sub> (Figure S3).

**Electronic Absorption Spectroscopy.** The absorption spectrum of **1** in dichloromethane shows an absorption band at 368 nm ( $\varepsilon = 14700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), and a dichloromethane solution of **2** shows a shoulder at 410 nm ( $\varepsilon = 11000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) (Figure S4). Both spectra did not change with time, suggesting that tetranuclear structures of **1** and **2** are maintained in the solutions. A toluene solution of **1** showed an absorption band at 372 nm similar to that of a dichloromethane solution of **1**, while such a band was not observed for a methanol solution of **1**. This suggests that complex **1** is not stable in methanol. On the other hand, the absorption spectrum of a methanol solution of **2** gradually changed: the shoulder at 410 nm decreased and a new band appeared at 580 nm after 50 h (Figure S5). The solution behavior of **1** and **2** was further investigated by ESI mass spectrometry (*vide infra*).

**ESI Mass Spectrometry.** ESI mass spectra of **1** and **2** were measured in dichloromethane, acetonitrile, or methanol in the positive mode. In the ESI mass spectrum of dichloromethane solutions, two low intensity signals were detected for **1** (Figure S6). These two signals are assignable to  $[Mn_4(L)_2(OAc)]^+$  (*m*/*z* 1399) and

 $[Mn_4(L)_2(OAc)_2]^+$  (*m*/*z* 1458). Complex **1** is insoluble in acetonitrile, while **2** is soluble. The ESI mass spectrum of **2** in acetonitrile exhibits the signal attributed to the doubly charged ion  $[Mn_4(L)_2Cl_2]^{2+}$  at *m*/*z* 705 (Figure S7). The signal for  $[Mn_4(L)_2Cl_3]^+$  was also observed at *m*/*z* 1447 as the base peak. This suggests that the tetramanganese structure of **2** is retained in acetonitrile.

The ESI mass spectrum of **1** in methanol shows the signal for  $[Mn_2(L_2H_3)]^+$  (*m/z* 1233), in which two acetate and two manganese ions are removed from **1** (Figure S8). After 7 days, a new signal for  $[Mn_2(L)(OCH_3)]^+$  appeared at *m/z* 701 (Figure S9). The ESI mass spectrum of **2** in methanol shows a dominant signal for  $[Mn_2(L)(OCH_3)]^+$  at *m/z* 701 (Figure S10), which suggests dissociation of the chloride ligands, followed by monomerization. After 3 days, new signals including  $[Mn_2(L_2H_2)]^+$  (*m/z* 1232) and  $[Mn_2(L_2H_3)]^+$  (*m/z* 1233) were observed (Figure S11). This indicates that the absorption spectral change of a methanol solution of **2** is related to the partial dissociation of manganese ions from the Mn\_2(L) units (vide supra).

X-Ray Crystal Structure Determination of 1 and 2. A single crystal of 1 or 2 was mounted on a glass fiber. The diffraction data were collected on an AFC7/CCD Mercury diffractometer. The data were processed and corrected for Lorentz and polarization effects using CrystalClear software.<sup>2</sup> Absorption corrections were applied using the Multi Scan method. The structures were solved using direct methods (SIR97<sup>3</sup>) and refined by full-matrix least-squares on  $F^2$  using SHELXL-97.<sup>4</sup> Crystallographic data are summarized in Table S1. The structures of 1 and 2 are shown in Figures S12 and S13, respectively. Selected bond distances and angles for 1 and 2 are listed in Tables S2 and S3, respectively.

## References

- (1) Hirotsu, M.; Ohno, N.; Nakajima, T.; Kushibe, C.; Ueno, K.; Kinoshita, I. *Dalton Trans.* **2010**, *39*, 139–148.
- (2) CrystalClear, Rigaku Corporation, 2001.
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- (4) Sheldrick, G. M. SHELX-97, Program for the Solution and Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997.



**Figure S1.** Temperature dependence of  $\chi T$  for **1** ( $\circ$ ) and **2** ( $\Box$ ). Solid lines represent the least-squares fits of the data to the model described in the text.



**Figure S2.** Cyclic voltammograms of **1**  $(1 \times 10^{-4} \text{ M})$  in dichloromethane containing 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> (--, ---); scan rate, 100 mV s<sup>-1</sup>; working electrode, glassy carbon; auxiliary electrode, platinum wire; reference electrode, Ag/Ag<sup>+</sup>.



**Figure S3.** Cyclic voltammograms of **2**  $(1 \times 10^{-3} \text{ M})$  in dichloromethane containing 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> (—, ---) and Bu<sub>4</sub>NCl (—); scan rate, 100 mV s<sup>-1</sup>; working electrode, glassy carbon; auxiliary electrode, platinum wire; reference electrode, Ag/Ag<sup>+</sup>.



Figure S4. Absorption spectra of 1 (—) and 2 (—) in dichloromethane.



**Figure S5.** Absorption spectral changes of **2** in methanol: 0 h (—); 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 26 h (—); 50 h (—).



**Figure S6.** (a) ESI mass spectrum of **1** in dichloromethane. (b) Expanded view of the region from m/z 1380 to 1480. (c) Calculated isotopic distribution patterns for  $[Mn_4(L)_2(OAc)]^+$  (m/z 1399) (left) and  $[Mn_4(L)_2(OAc)_2]^+$  (m/z 1458) (right).

![](_page_9_Figure_0.jpeg)

Figure S7. (a) ESI mass spectrum of 2 in acetonitrile. (b) Expanded view of the region from m/z 670 to 720 (left) and the calculated isotopic distribution pattern for  $[Mn_4(L)_2Cl_2]^{2+}$  (m/z 705) (right). (c) Expanded view of the signal attributed to  $[Mn_4(L)_2Cl_3]^+$  (*m*/*z* 1447) (left) and the calculated isotopic distribution pattern (right).

(a)

![](_page_10_Figure_0.jpeg)

**Figure S8.** (a) ESI mass spectrum of **1** in methanol. (b) Expanded view of the signal attributed to  $[Mn_2(L_2H_3)]^+$  (*m*/*z* 1233) (left) and the calculated isotopic distribution pattern (right).

![](_page_11_Figure_0.jpeg)

Figure S9. (a) ESI mass spectrum of **1** in methanol after 7 days. (b) Expanded view of the region from m/z 670 to 720 (left) and the calculated isotopic distribution pattern for  $[Mn_2(L)(OCH_3)]^+$  (m/z 701) (right). (c) Expanded view of the signal attributed to  $[Mn_2(L_2H_2)]^+$  (*m*/*z* 1232) and  $[Mn_2(L_2H_3)]^+$  (*m*/*z* 1233) (left) and the calculated isotopic distribution pattern for a 1:3 mixture of  $[Mn_2(L_2H_2)]^+$  and  $[Mn_2(L_2H_3)]^+$  (right).

![](_page_12_Figure_0.jpeg)

Figure S10. (a) ESI mass spectrum of 2 in methanol. (b) Expanded view of the signal attributed to  $[Mn_2(L)(OCH_3)]^+$  (m/z 701) (left) and the calculated isotopic distribution pattern (right).

![](_page_13_Figure_0.jpeg)

Figure S11. (a) ESI mass spectrum of 2 in methanol after 3 days. (b) Expanded view of the region from m/z 670 to 720 (left) and the calculated isotopic distribution pattern for  $[Mn_2(L)(OCH_3)]^+$  (m/z 701) (right). (c) Expanded view of the signal attributed to  $[Mn_2(L_2H_2)]^+$  (*m*/*z* 1232) and  $[Mn_2(L_2H_3)]^+$  (*m*/*z* 1233) (left) and the calculated isotopic distribution pattern for a 7:3 mixture of  $[Mn_2(L_2H_2)]^+$  and  $[Mn_2(L_2H_3)]^+$  (right).

(a)

	1	2
Empirical formula	$C_{84}H_{94}Cl_8Mn_4N_4O_{16}\\$	$C_{70}H_{80}Cl_4Mn_4N_4O_{18}\\$
Formula weight	1918.99	1626.94
Temperature/K	163	120
Wavelength/Å	0.7107	0.7107
Crystal system	triclinic	orthorhombic
Space group	PĪ	<i>C</i> 222 <sub>1</sub>
a/Å	12.384(2)	13.7200(19)
b/Å	13.3307(19)	33.820(5)
$c/ m \AA$	15.2393(14)	15.370(2)
$lpha'^\circ$	65.483(11)	90
$eta\!\!/^{\circ}$	70.914(12)	90
$\gamma^{\prime \circ}$	83.701(15)	90
$V/\text{\AA}^3$	2162.2(5)	7131.8(18)
Ζ	1	4
$D_{ m calcd}/ m Mg{\cdot}m^{-3}$	1.474	1.515
$\mu$ (Mo K $\alpha$ )/mm <sup>-1</sup>	0.885	0.915
<i>F</i> (000)	990	3360
Crystal size/mm <sup>3</sup>	$0.37 \times 0.11 \times 0.07$	$0.15 \times 0.15 \times 0.10$
Reflections collected	21110	26876
Independent reflections	9306 ( $R_{\rm int} = 0.039$ )	7972 ( $R_{\rm int} = 0.071$ )
Completeness to $\theta$	95.4% ( <i>θ</i> = 25.0°)	98.1% ( <i>θ</i> = 27.46°)
Max. and min. transmission	0.9407 and 0.7355	0.9141 and 0.8750
No. of data/restraints/parameters	9306/1/622	7972/0/476
Goodness of fit on $F^2$	1.087	1.161
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0713	R1 = 0.0795
<i>R</i> indices (all data)	wR2 = 0.1728	wR2 = 0.1677
Absolute structure parameter		-0.02(3)
Largest diff. peak and hole $(e \cdot Å^{-3})$	1.50 and -1.18	0.402 and -0.644

 Table S1.
 Crystallographic data for 1 and 2

![](_page_15_Figure_0.jpeg)

**Figure S12.** ORTEP drawings of **1** with thermal ellipsoids at the 50% probability level. (a) Structure of  $[Mn_4(L)_2(\mu$ -OAc)\_2]. Hydrogen atoms are omitted for clarity. (b) Tetaramanganese core structure in **1**. Solid bonds represent the incomplete double-cubane structure of  $Mn_4O_6$ .

Tuble 52. Beleeted be	Sha distances/11 and		
Mn(1)–O(1)	2.073(3)	Mn(2)–O(1)	2.360(3)
Mn(1)–O(2)	2.124(3)	Mn(2)–O(2)*	1.907(3)
Mn(1)–O(4)	2.317(3)	Mn(2)–O(3)	1.868(3)
Mn(1)–O(4)*	2.234(3)	Mn(2)–O(4)	1.947(3)
Mn(1)–O(6)	2.166(3)	Mn(2)–O(7)*	2.207(3)
Mn(1)–N(1)	2.202(3)	Mn(2)–N(2)	2.023(3)
$Mn(1)\cdots Mn(1)^*$	3.4020(13)	$Mn(1)\cdots Mn(2)$	3.3780(10)
Mn(1)····Mn(2)*	3.0963(9)	Mn(2)····Mn(2)*	5.5156(14)
O(1)-Mn(1)-O(2)	161.44(11)	O(1)-Mn(2)-O(2)*	90.70(11)
O(1)-Mn(1)-O(4)	76.21(10)	O(1)–Mn(2)–O(3)	99.66(11)
O(1)-Mn(1)-O(4)*	108.84(10)	O(1)-Mn(2)-O(4)	77.51(11)
O(1)-Mn(1)-O(6)	102.85(11)	O(1)-Mn(2)-O(7)*	166.72(11)
O(1)-Mn(1)-N(1)	87.03(11)	O(1)-Mn(2)-N(2)	90.73(12)
O(2)–Mn(1)–O(4)	85.92(10)	O(2)*-Mn(2)-O(3)	92.45(12)
O(2)-Mn(1)-O(4)*	73.36(10)	O(2)*-Mn(2)-O(4)	85.02(11)
O(2)-Mn(1)-O(6)	95.67(11)	O(2)*-Mn(2)-O(7)*	90.76(12)
O(2)–Mn(1)–N(1)	91.87(11)	O(2)*-Mn(2)-N(2)	177.77(13)
O(4)-Mn(1)-O(4)*	83.26(10)	O(3)-Mn(2)-O(4)	176.16(13)
O(4)–Mn(1)–N(1)	101.88(12)	O(3)-Mn(2)-O(7)*	93.46(12)
O(4)*-Mn(1)-N(1)	164.11(11)	O(3)-Mn(2)-N(2)	89.00(13)
O(6)-Mn(1)-O(4)	168.25(10)	O(4)-Mn(2)-O(7)*	89.47(11)
O(6)-Mn(1)-O(4)*	86.04(10)	O(4)-Mn(2)-N(2)	93.62(12)
O(6)–Mn(1)–N(1)	89.72(12)	O(7)*-Mn(2)-N(2)	87.45(12)
Mn(1)–O(1)–Mn(2)	99.05(11)	Mn(1)*-O(4)-Mn(2)	95.30(11)
Mn(1)-O(2)-Mn(2)*	100.25(12)	Mn(1)-O(4)-Mn(2)	104.44(12)
Mn(1)–O(4)–Mn(1)*	96.74(10)		

 Table S2.
 Selected bond distances/Å and angles/° for 1

![](_page_17_Figure_0.jpeg)

Figure S13. ORTEP drawings of 2 with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. (a) Side and (b) top views. The Cl1 and O1 atoms were found to be split over two positions related by the  $C_2$  axis, and they were refined with occupancies of 0.5 each.

Table 55. Selected b	ond distances/A ar	id angles/ for Z	
Mn(1)–O(1)	2.032(14)	Mn(2)–O(3)	1.971(4)
Mn(1)–O(2)	1.882(4)	Mn(2)–O(4)	1.863(4)
Mn(1)–O(3)	1.935(4)	Mn(2)–O(5)	1.939(4)
Mn(1)–O(5)	1.943(4)	Mn(2)–N(2)	2.010(5)
Mn(1)–N(1)	2.021(5)	Mn(2)–Cl(2)	2.4572(18)
Mn(1)–Cl(1)	2.582(6)	Mn(2)–Cl(3)	2.9374(15)
Mn(1)–Cl(3)	2.7355(16)		
Mn(1)–Mn(2)	2.9137(12)	Mn(1)–Mn(2)*	5.6689(14)
Mn(1)–Mn(1)*	4.768(2)	Mn(2)–Mn(2)*	4.9697(19)
Cl(1)–Mn(1)–Cl(3)	170.16(14)	Cl(2)–Mn(2)–Cl(3)	168.54(6)
Cl(1)–Mn(1)–O(2)	95.8(2)	Cl(2)-Mn(2)-O(3)	96.68(12)
Cl(1)–Mn(1)–O(3)	90.73(18)	Cl(2)-Mn(2)-O(4)	97.98(14)
Cl(1)-Mn(1)-O(5)	96.44(17)	Cl(2)-Mn(2)-O(5)	95.44(13)
Cl(1)–Mn(1)–N(1)	88.83(19)	Cl(2)-Mn(2)-N(2)	93.16(16)
Cl(3)–Mn(1)–O(2)	93.97(16)	Cl(3)–Mn(2)–O(3)	73.80(11)
Cl(3)–Mn(1)–O(3)	79.43(12)	Cl(3)-Mn(2)-O(4)	89.02(14)
Cl(3)–Mn(1)–O(5)	81.79(13)	Cl(3)-Mn(2)-O(5)	76.56(12)
Cl(3)–Mn(1)–N(1)	92.20(15)	Cl(3)-Mn(2)-N(2)	95.74(15)
O(2)-Mn(1)-O(3)	169.96(18)	O(3)–Mn(2)–O(4)	92.95(17)
O(2)-Mn(1)-O(5)	92.92(18)	O(3)–Mn(2)–O(5)	77.93(16)
O(2)-Mn(1)-N(1)	91.30(19)	O(3)–Mn(2)–N(2)	168.59(18)
O(3)-Mn(1)-O(5)	78.73(16)	O(4)-Mn(2)-O(5)	164.57(19)
O(3)-Mn(1)-N(1)	96.48(18)	O(4)-Mn(2)-N(2)	91.37(19)
O(5)-Mn(1)-N(1)	172.88(19)	O(5)-Mn(2)-N(2)	95.45(18)
O(1)–Mn(1)–Cl(3)	171.7(4)		
O(1)-Mn(1)-O(2)	89.7(4)	Mn(1)–O(5)–Mn(2)	97.30(17)
O(1)-Mn(1)-O(3)	95.9(4)	Mn(1)-Cl(3)-Mn(1)*	121.28(9)
O(1)-Mn(1)-O(5)	90.7(4)	Mn(1)–Cl(3)–Mn(2)	61.69(3)
O(1)-Mn(1)-N(1)	95.1(4)	Mn(1)-Cl(3)-Mn(1)*	121.28(9)
		Mn(1)-Cl(3)-Mn(2)*	175.70(6)
Mn(1)–O(3)–Mn(2)	96.48(15)	Mn(2)-Cl(3)-Mn(2)*	115.54(8)

**Table S3.** Selected bond distances/Å and angles/° for **2**