

Supporting information for

**Supersilyl as an Effective Monodentate Spectator
Ligand to Stabilize Four-Coordinate
Manganese(II) Complexes**

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General. Manipulation of air and moisture sensitive compounds was carried out under a dry nitrogen atmosphere using Schlenk tube techniques associated with a high-vacuum line or in the glove box which was filled with dry nitrogen. All solvents were distilled purchased from Kanto Chemical Co. Inc., and was dried over activated molecular sieves. ^1H and ^{13}C NMR spectra were recorded on a JEOL Lambda 400 spectrometer at ambient temperature. ^1H and ^{13}C NMR chemical shifts (δ values) were given in ppm relative to the solvent signals. Elemental analyses for complexes **2** and **4** were performed by a Thermo Scientific FLASH 2000 Organic Elemental Analyzer, and Elemental analyses for complexes **3** and **5** were performed at the A Rabbit Science Co., Ltd. IR spectrum was recorded on a PerkinElmer Spectrum Two spectrometer. Magnetic susceptibility data of the solid samples were measured on Quantum Design MPMS-XL7. Dc magnetic susceptibility measurements were carried out under the applied field of 0.1 T in the temperature range of 1.9–300 K. Potassium tris(trimethylsilyl)silanide was synthesized by the method reported in the literature.¹ All reagents were purchased from Tokyo Chemical Industries Co., Ltd., Sigma-Aldrich or Kanto Chemical Co., Inc. and were used without further purification.

Synthesis of $\{[\text{Si}(\text{SiMe}_3)_3](\text{THF})\text{Mn}(\mu\text{-Br})\}_2$ (2**).** In a 50 mL schlenk tube, MnBr_2 (1 g, 4.66 mmol) was suspended in THF (20 mL), then potassium tris(trimethylsilyl)silanide, generated from the reaction of $\text{Si}(\text{SiMe}_3)_4$ (1.57 g, 4.89 mmol) with KO^tBu (548.6 mg, 4.89 mmol) in THF (20 mL), was slowly added to this solution at room temperature. The solution was stirred at room temperature for 1 h. Then the solution was centrifuged to remove the insoluble materials. The mother liquid was evaporated *in vacuo*, and the obtained solid was dissolved in pentane (60 mL). The solution was again centrifuged to remove the insoluble materials. The supernatant was collected, and concentrated to ca. 20 mL. The remaining solution was cooled at $-20\text{ }^\circ\text{C}$ to afford complex **2** as colorless crystals in 72% yield (1.52 g, 1.67 mmol). ^1H NMR (400 MHz, r.t., C_6D_6): δ = 4.78 (brs, 54H, SiMe_3), 14.99 (brs, 8H, THF), 35.77 (brs, 8H, THF). Magnetic susceptibility (Evans): $\mu_{\text{eff}} = 6.52$ (in C_6D_6 , $21\text{ }^\circ\text{C}$). Anal. Calcd. for $\text{C}_{26}\text{H}_{70}\text{O}_2\text{Si}_8\text{Mn}_2\text{Br}_2$: C, 34.35; H, 7.76. Found: C, 34.05; H, 7.63.

Synthesis of $\{[\text{Si}(\text{SiMe}_3)_3](\text{THF})\text{Mn}(\mu\text{-O}^t\text{Bu})\}_2$ (3**).** In a 10 mL schlenk tube, complex **2** (100 mg, 0.11 mmol) was dissolved in THF (3 mL), then KO^tBu (24.6 mg, 0.22 mmol) in THF (5 mL) was added to this solution at room temperature. The solution was stirred at room temperature for overnight. The solvent was removed *in vacuo*, then the remaining product was extracted with pentane (20 mL). The solution was centrifuged to remove the insoluble materials. The supernatant was collected, and the solvent was concentrated to ca. 2 mL. The remaining solution was cooled at $-30\text{ }^\circ\text{C}$, then **3** was obtained as colorless crystals in 85 % yield (84 mg, 0.08 mmol). ^1H NMR (400 MHz, r.t., C_6D_6): δ = 3.29 (brs). Magnetic susceptibility (Evans): $\mu_{\text{eff}} = 6.78$ (in C_6D_6 , $20\text{ }^\circ\text{C}$). Anal. Calcd. for $\text{C}_{34}\text{H}_{88}\text{O}_4\text{Si}_8\text{Mn}_2$: C, 45.60; H, 9.90. Found: C, 45.59; H, 10.59.

Complex **3** can also be synthesized as follows: In a 50 mL schlenk tube, MnBr_2 (140.0 mg, 0.65 mmol) was suspended in THF (20 mL), then THF (10 mL) solution of $\text{K}[\text{Si}(\text{SiMe}_3)_3] \cdot 1.0\text{THF}$ (250.0 mg, 0.70 mmol) was added to this solution at room temperature. The solution was stirred at room temperature for 3 h, then KO^tBu (73.0 mg, 0.65 mmol) was added to this solution. The obtained solution was stirred at room temperature for overnight. The solvent was removed *in vacuo*, then the remaining product was extracted with pentane (40 mL). The solution was centrifuged to remove the insoluble materials. The supernatant was collected, and the

solvent was concentrated to ca. 5 mL. The remaining solution was cooled at -30 °C, then **3** was obtained as colorless crystals in 79 % yield (231.8 mg, 0.26 mmol).

Synthesis of $\{\text{Si}(\text{SiMe}_3)_3\}(\text{iPr}_2\text{IM}^{\text{Me}})_2\text{MnMe}$ (4**).** In a 10 mL schlenk tube, complex **2** (200 mg, 0.22 mmol) was dissolved in THF (20 mL), then $\text{iPr}_2\text{IM}^{\text{Me}}$ (160.8 mg, 0.88 mmol) was added to this solution at room temperature. The solution was stirred at room temperature for 1 h. In the course of the reaction, the color of the solution was changed from colorless to pale yellow. The obtained solution was cooled to -78 °C, then 1.18 mL (1.32 mmol) of MeLi (1.12 M diethyl ether solution) was added. The solution was stirred at room temperature for overnight, then the solvent was removed *in vacuo*. The remaining product was extracted with diethyl ether (20 mL), then the solution was centrifuged to remove the insoluble materials. The supernatant was collected, and the solvent was concentrated to ca. 8 mL. The remaining solution was cooled at -20 °C, then **4** was obtained as pale pink crystals in 53 % yield (157.7 mg, 0.233 mmol). ^1H NMR (400 MHz, r.t., C_6D_6): $\delta = 5.61$ (brs), 18.74 (brs). Magnetic susceptibility (Evans): $\mu_{\text{eff}} = 7.11$ (in C_6D_6 , 21 °C). Anal. Calcd. for $\text{C}_{32}\text{H}_{70}\text{N}_4\text{Si}_4\text{Mn}$: C, 56.67; H, 10.40; N, 8.26. Found: C, 56.53; H, 10.53; N, 8.32.

Synthesis of $[\{\text{Si}(\text{SiMe}_3)_3\}(\text{iPr}_2\text{IM}^{\text{Me}})\text{Mn}(\text{m-H})]_2$ (5**).** In a 10 mL schlenk tube, complex **2** (454.6 mg, 0.50 mmol) was dissolved in THF (20 mL), then $\text{iPr}_2\text{IM}^{\text{Me}}$ (364.6 mg, 2.02 mmol) was added to this solution at room temperature. The solution was stirred at room temperature for 1 h. In the course of the reaction, the color of the solution was changed from colorless to pale yellow. The obtained solution was cooled to -78 °C, then 1.0 mL (1.0 mmol) of NaBEt_3H (1.0 M THF solution) was added. The solution was stirred at room temperature for overnight, then the solvent was removed *in vacuo*. The remaining product was extracted with diethyl ether (50 mL), then the solution was centrifuged to remove the insoluble materials. The supernatant was collected, and the solvent was concentrated to ca. 30 mL. The remaining solution was cooled at -20 °C, then **5** was obtained as brown crystals in 58 % yield (282.8 mg, 0.292 mmol). ^1H NMR (400 MHz, r.t., C_6D_6): $\delta = 2.75$ (brs), 16.13 (brs). IR(ATR): 2978, 2955, 2930, 2898, 1629, 1550, 1457, 1399, 1374, 1340, 1245, 1208, 1198, 1140, 1105, 1012, 819, 751, 667, 619, 595, 569, 531 cm^{-1} . Magnetic susceptibility (Evans): $\mu_{\text{eff}} = 5.05$ (in C_6D_6 , 21 °C). Anal. Calcd. for $\text{C}_{40}\text{H}_{96}\text{N}_4\text{Si}_8\text{Mn}_2$: C, 49.64; H, 10.00; N, 5.79. Found: C, 49.64; H, 10.31; N, 5.51.

Figure S1. ^1H NMR spectrum of **2** in C_6D_6 at room temperature.

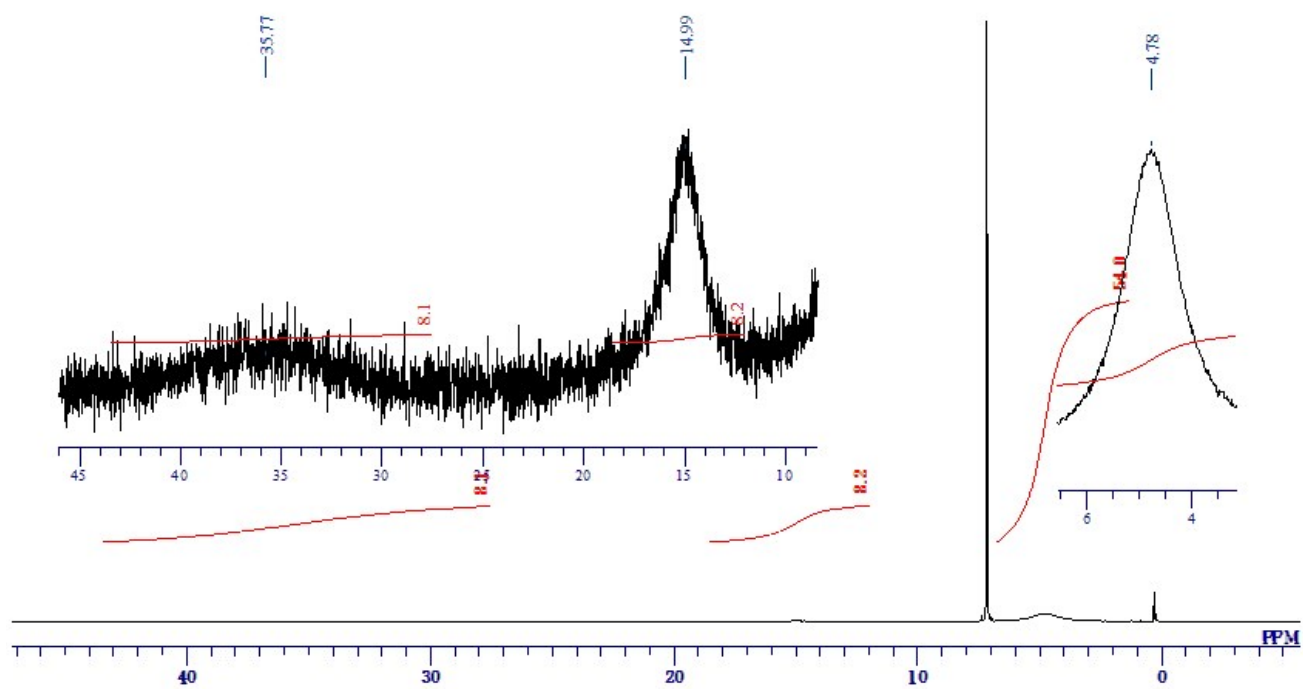


Figure S2. ^1H NMR spectrum of **3** in C_6D_6 at room temperature.

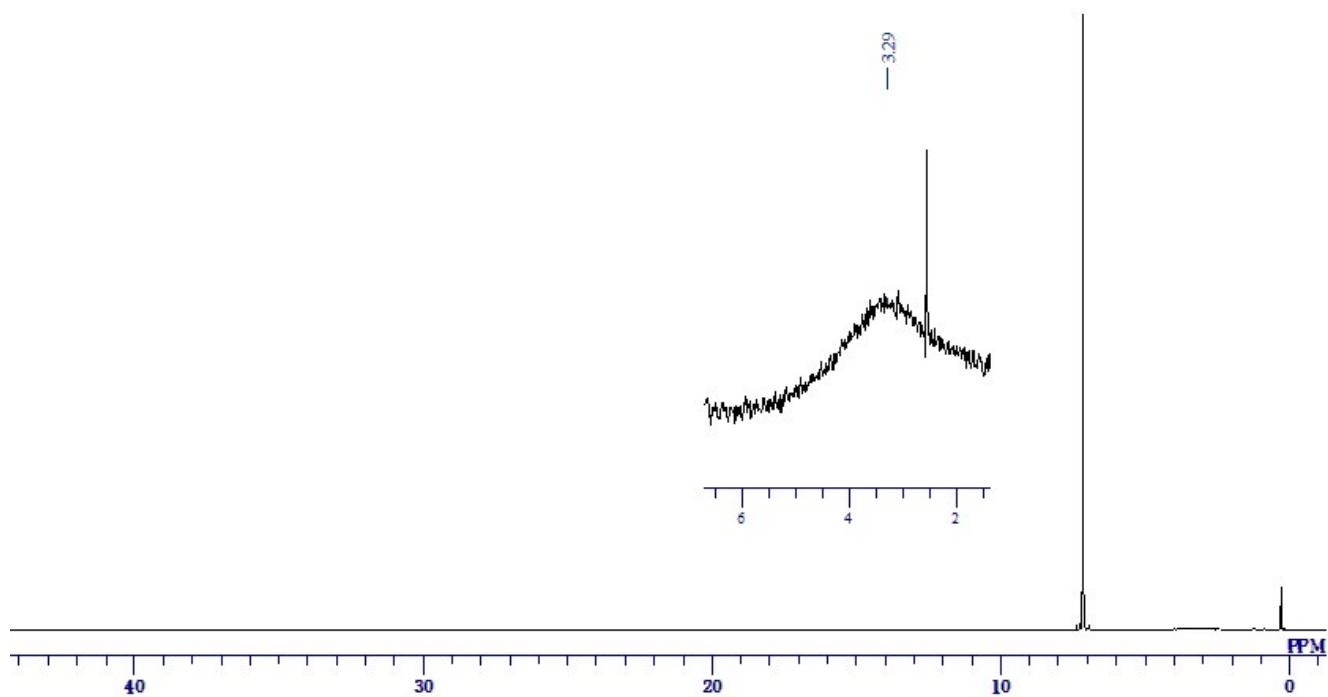


Figure S3. ^1H NMR spectrum of **4** in C_6D_6 at room temperature.

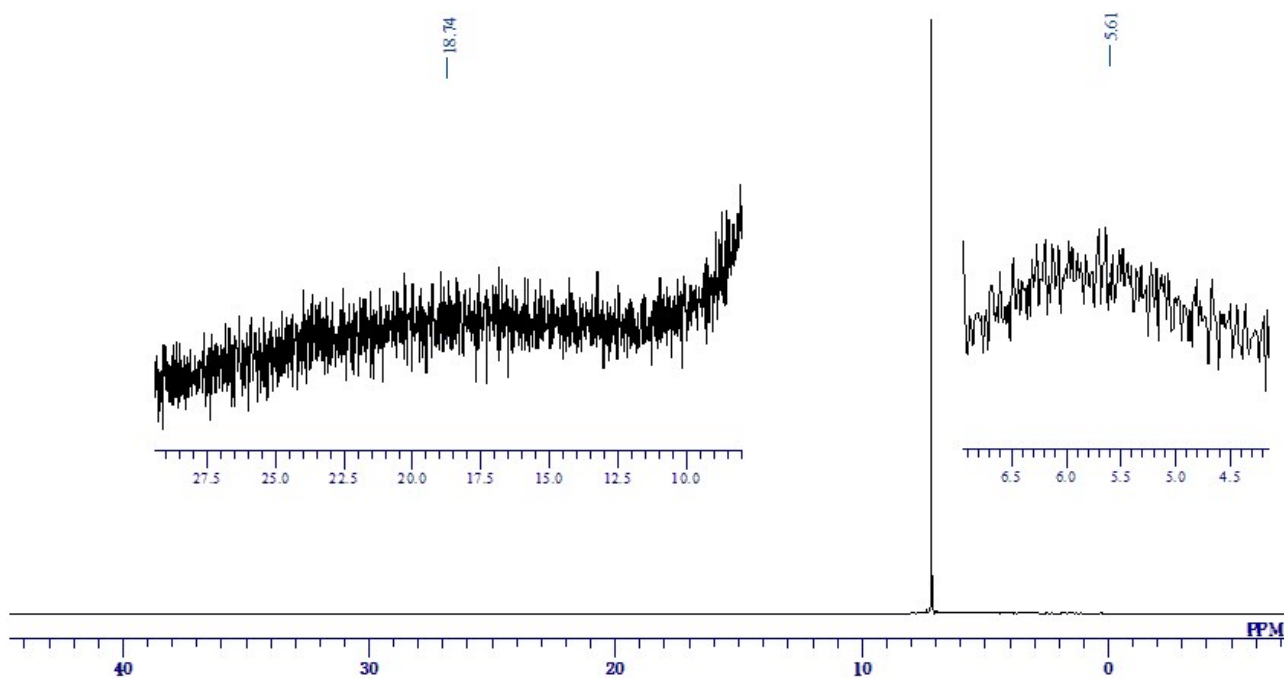


Figure S4. ^1H NMR spectrum of **5** in C_6D_6 at room temperature.

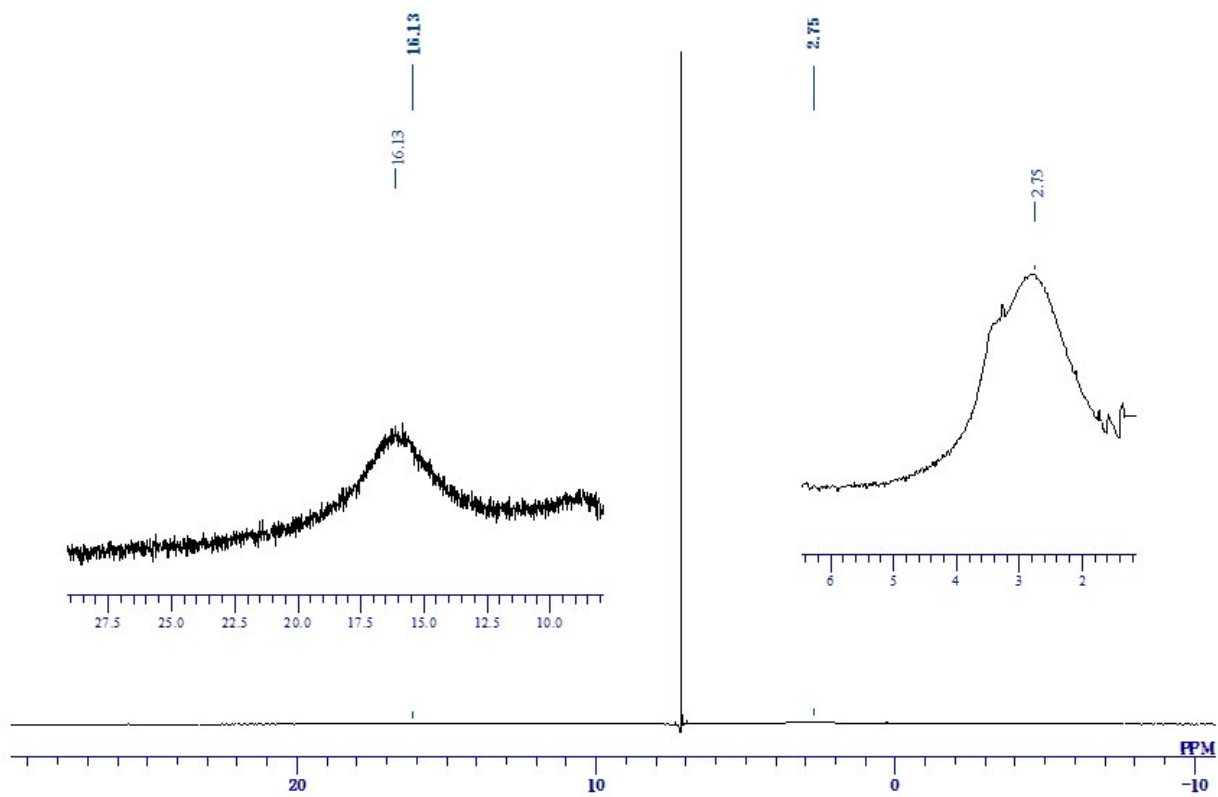
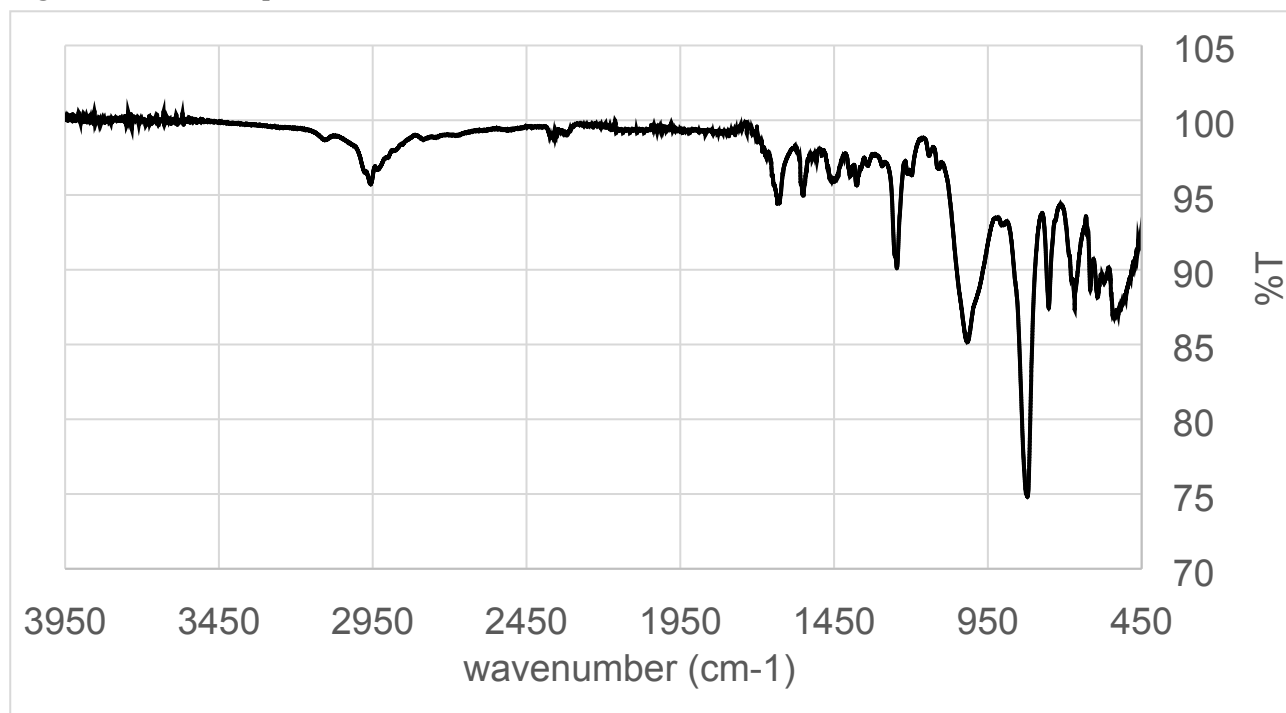


Figure S5. ATR-IR spectrum of **5** in the solid state.



Magnetic susceptibilities

Magnetic susceptibilities of solid samples were measured using a Quantum Design MPMS-XL7. Direct current (dc) field-cooling magnetic susceptibility measurements were carried out between 1.9 and 300 K under 0.1 T magnetic field. Diamagnetic corrections were applied by the diamagnetism of the sample holder. The magnetic interactions were analyzed by fitting the temperature-dependence of magnetic susceptibilities in the temperature range of 20-300 K with the following isotropic spin Heisenberg–Dirac–van Vleck Hamiltonian

$$H = -2JS_{Mn1}S_{Mn2}$$

where J represent the exchange constants of two manganese centers. The g values for Mn(II) was fixed to 2. The analyses were carried out by using the PHI program.²

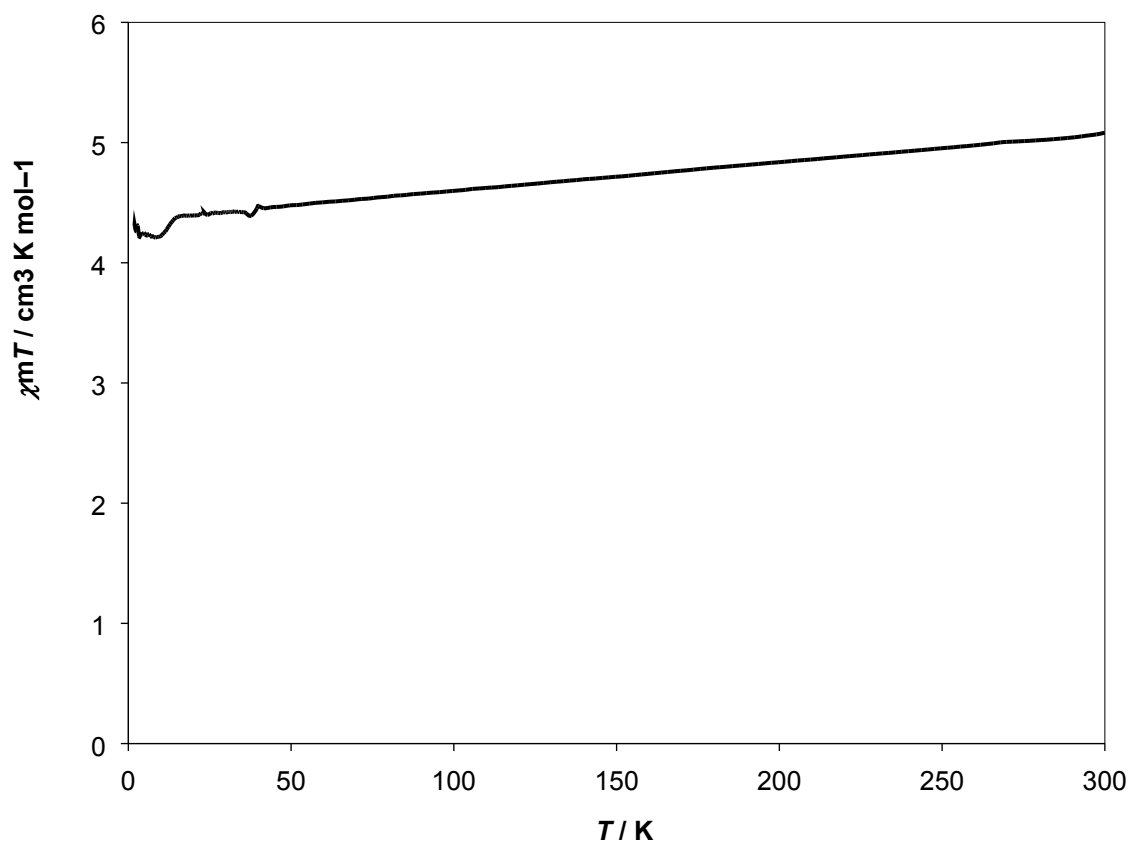


Figure S6-1. Temperature dependences of $\chi_m T$ for **1** under the applied dc field of 0.1 T.

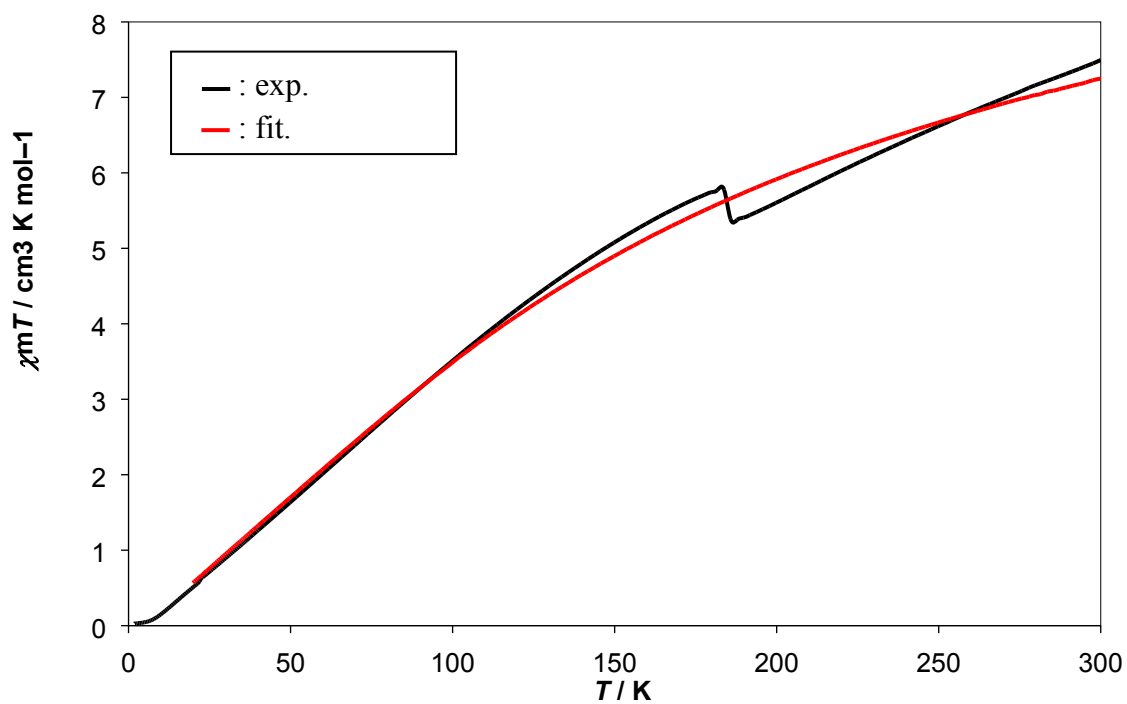


Figure S6-2. Temperature dependences of $\chi_m T$ for **2** under the applied dc field of 0.1 T. The solid line represents the best fit adopting the Heisenberg–Dirac–Van Vleck Hamiltonian.

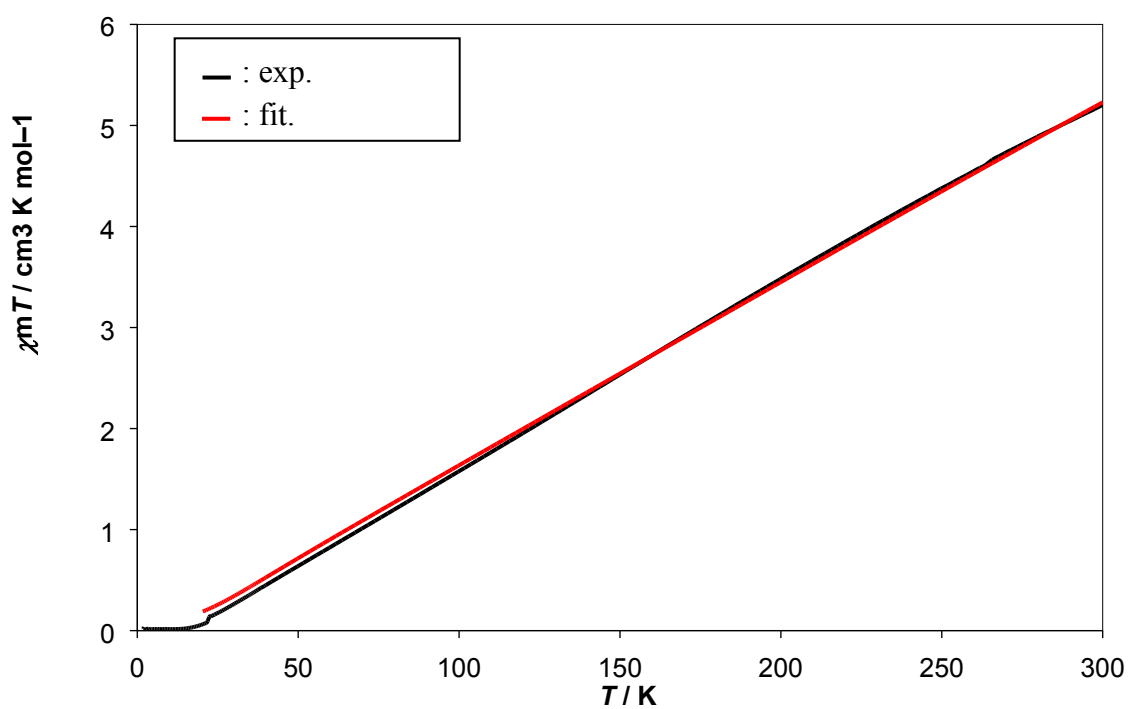


Figure S6-3. Temperature dependences of $\chi_m T$ for **5** under the applied dc field of 0.1 T. The solid line represents the best fit adopting the Heisenberg–Dirac–Van Vleck Hamiltonian.

X-ray data collection and reduction

X-ray crystallography was performed on a Rigaku Saturn CCD area detector with graphite monochromated Mo-K α radiation ($\lambda=0.71075$ Å). The data were collected at 213 K for **2**, 243 K for **3**, and 203 K for **4** and **5** using ω scan in the θ range of $3.14 \leq \theta \leq 27.49$ deg (**2**), $3.01 \leq \theta \leq 27.49$ deg (**3**), $3.17 \leq \theta \leq 27.48$ deg (**4**) and $3.03 \leq \theta \leq 27.49$ deg (**5**). The data obtained were processed using Crystal-Clear (Rigaku) on a Pentium computer, and were corrected for Lorentz and polarization effects. The structures were solved by direct methods³, and expanded using Fourier techniques. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 5517 observed reflections and 181 variable parameters for **2**, 6162 observed reflections and 212 variable parameters for **3**, 9686 observed reflections and 370 variable parameters for **4** and 7644 observed reflections and 248 variable parameters for **5**. Neutral atom scattering factors were taken from International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4⁴. Anomalous dispersion effects were included in F_{calc} ⁵; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley⁶. The values for the mass attenuation coefficients are those of Creagh and Hubbell⁷. All calculations were performed using the CrystalStructure⁸ crystallographic software package except for refinement, which was performed using SHELXL Version 2017/1⁹. Details of final refinement as well as the bond lengths and angle are summarized in Tables S1, S2, S3 and S4 and the numbering scheme employed is also shown in Figures S7, S8, S9 and S10 which were drawn with ORTEP at 50% probability ellipsoids. CCDC 2026301 (**2**), 2026302 (**3**), 2026303 (**4**) and 2026304 (**5**) contain the supplementary crystallographic data for this paper.

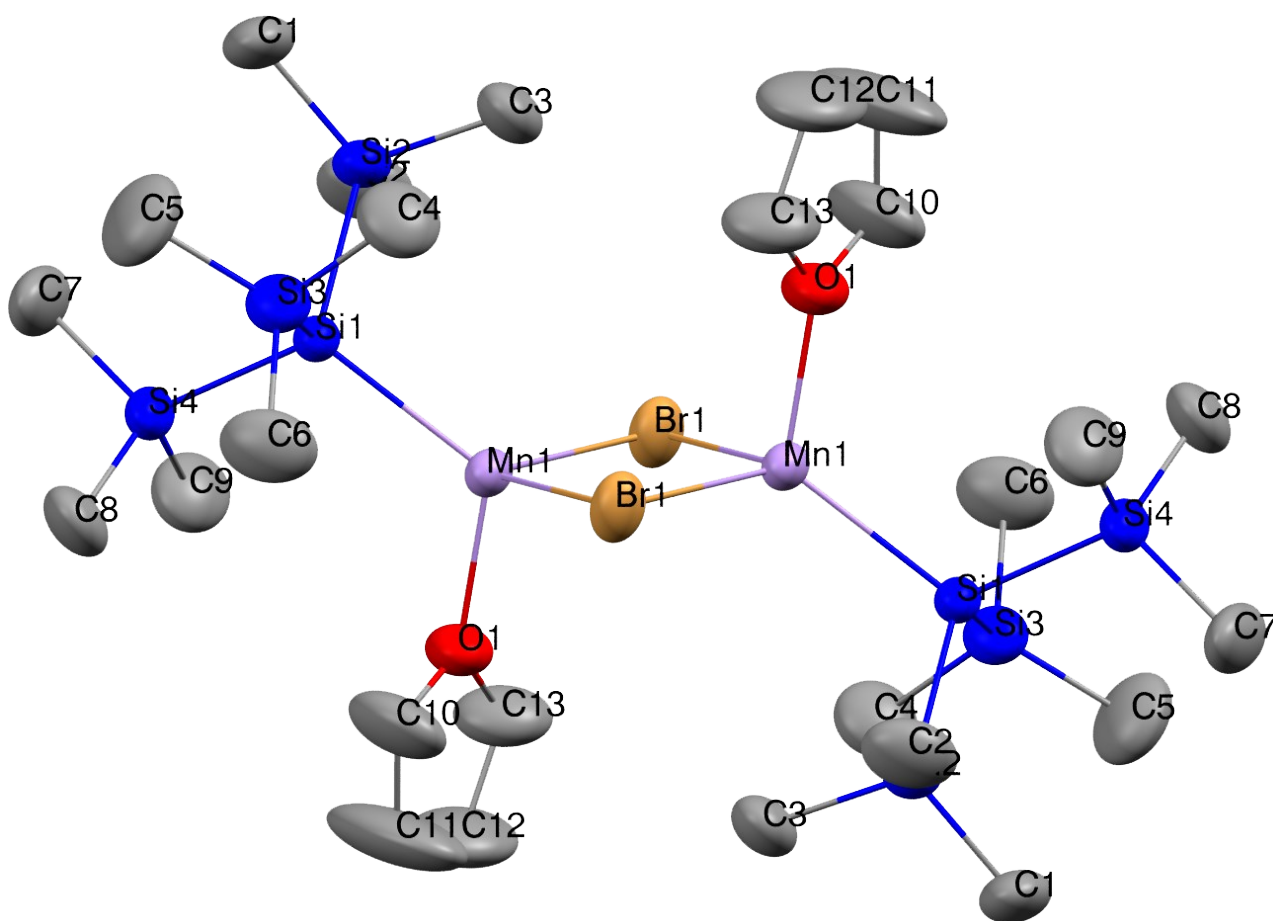


Figure S7. ORTEP drawing of **2** (50% probability of the thermal ellipsoids)

Table S1-1. Crystal data and structure refinement for **2**.

Empirical Formula	C ₂₆ H ₇₀ Br ₂ Mn ₂ O ₂ Si ₈
Formula Weight	909.21
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.200 X 0.150 X 0.150 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 9.482(4) Å b = 10.595(4) Å c = 13.023(5) Å α = 90.848(4) ° β = 107.188(5) ° γ = 96.065(5) ° V = 1241.4(8) Å ³
Space Group	P-1 (#2)
Z value	1
D _{calc}	1.216 g/cm ³
F ₀₀₀	474.00
μ(MoKα)	23.347 cm ⁻¹
Diffractionmeter	Saturn724
Radiation	MoKα (λ = 0.71075 Å) multi-layer mirror monochromated
Voltage, Current	50kV, 24mA
Temperature	-60.0°C
Detector Aperture	72.8 x 72.8 mm
Data Images	2880 exposures
ω oscillation Range (χ=45.0, φ=0.0)	-70.0 - 110.0°
Exposure Rate	4.0 sec./°
Detector Swing Angle	19.89°
ω oscillation Range (χ=45.0, φ=90.0)	-70.0 - 110.0°
Exposure Rate	4.0 sec./°
Detector Swing Angle	19.89°
ω oscillation Range (χ=45.0, φ=180.0)	-70.0 - 110.0°
Exposure Rate	4.0 sec./°
Detector Swing Angle	19.89°
ω oscillation Range (χ=45.0, φ=270.0)	-70.0 - 110.0°
Exposure Rate	4.0 sec./°
Detector Swing Angle	19.89°

Detector Position	44.68 mm
Pixel Size	0.141 mm
$2\theta_{\max}$	55.1°
No. of Reflections Measured	Total: 16571 Unique: 5517 ($R_{\text{int}} = 0.1137$)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.562 - 0.705)
Structure Solution	Direct Methods (SHELXT Version 2014/5)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1 / [\sigma^2(F_o^2) + (0.0396 \cdot P)^2 + 0.7005 \cdot P]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$
$2\theta_{\max}$ cutoff	55.1°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	5517
No. Variables	181
Reflection/Parameter Ratio	30.48
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0485
Residuals: R (All reflections)	0.0548
Residuals: wR_2 (All reflections)	0.1263
Goodness of Fit Indicator	1.071
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.70 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.62 e ⁻ /Å ³

Table S1-2. Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$ and occupancy

atom	x	y	z	B_{eq}
Br1	0.34727(3)	0.10070(3)	0.42660(2)	4.210(10)
Mn1	0.60006(5)	0.13430(4)	0.57317(3)	3.032(10)
Si1	0.63421(8)	0.25071(6)	0.75058(5)	2.709(13)
Si2	0.40014(9)	0.26902(8)	0.76981(7)	3.661(16)
Si3	0.76674(10)	0.13450(9)	0.89020(7)	4.104(17)
Si4	0.75857(10)	0.45538(8)	0.76239(7)	3.879(17)
O1	0.7368(3)	0.1991(3)	0.47801(19)	5.01(5)
C1	0.4034(5)	0.3192(5)	0.9089(4)	6.45(10)
C2	0.3067(5)	0.3874(5)	0.6747(4)	6.91(11)
C3	0.2786(5)	0.1142(4)	0.7335(4)	5.89(9)
C4	0.6563(5)	-0.0185(4)	0.8997(4)	6.37(10)
C5	0.8199(7)	0.2203(6)	1.0249(3)	7.90(13)
C6	0.9393(5)	0.0948(5)	0.8610(4)	7.05(11)
C7	0.7256(7)	0.5650(4)	0.8648(5)	7.74(14)
C8	0.9647(5)	0.4508(5)	0.7977(4)	6.88(11)
C9	0.6990(6)	0.5284(4)	0.6286(4)	6.90(11)
C10	0.8961(5)	0.1949(7)	0.5149(5)	9.29(18)
C11	0.9488(8)	0.2434(13)	0.4286(7)	16.8(5)
C12	0.8318(9)	0.2650(7)	0.3399(6)	10.5(2)
C13	0.6929(6)	0.2379(5)	0.3707(4)	7.09(11)

$$B_{\text{eq}} = 8/3 \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos \gamma + 2U_{13}(aa^*cc^*)\cos \beta + 2U_{23}(bb^*cc^*)\cos \alpha)$$

Table S1-3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br1	0.0551(2)	0.04282(17)	0.0560(2)	0.01674(13)	0.00385(13)	-0.00616(12)
Mn1	0.0448(2)	0.0348(2)	0.0377(2)	0.00067(16)	0.01709(16)	-0.00367(15)
Si1	0.0368(4)	0.0334(3)	0.0337(3)	0.0010(3)	0.0132(3)	-0.0009(3)
Si2	0.0446(4)	0.0488(4)	0.0525(5)	0.0047(3)	0.0254(3)	-0.0016(3)
Si3	0.0538(5)	0.0613(5)	0.0409(4)	0.0103(4)	0.0125(3)	0.0129(4)
Si4	0.0593(5)	0.0387(4)	0.0519(5)	-0.0104(4)	0.0266(4)	-0.0084(3)
O1	0.0620(14)	0.0787(16)	0.0555(13)	-0.0065(12)	0.0315(11)	0.0036(11)
C1	0.083(3)	0.097(3)	0.080(3)	-0.004(2)	0.053(2)	-0.021(2)
C2	0.066(3)	0.097(3)	0.116(4)	0.039(2)	0.041(2)	0.032(3)
C3	0.056(2)	0.078(3)	0.092(3)	-0.0151(19)	0.0347(19)	-0.009(2)
C4	0.096(3)	0.069(2)	0.081(3)	0.011(2)	0.029(2)	0.035(2)
C5	0.123(4)	0.120(4)	0.042(2)	0.022(3)	-0.001(2)	-0.001(2)
C6	0.068(3)	0.119(4)	0.089(3)	0.038(3)	0.023(2)	0.044(3)

C7	0.129(4)	0.066(2)	0.113(4)	-0.028(3)	0.071(3)	-0.044(3)
C8	0.062(2)	0.086(3)	0.110(3)	-0.027(2)	0.034(2)	-0.016(3)
C9	0.118(4)	0.058(2)	0.089(3)	-0.001(2)	0.039(3)	0.023(2)
C10	0.054(3)	0.192(7)	0.105(4)	-0.016(3)	0.031(2)	0.026(4)
C11	0.093(5)	0.412(18)	0.142(7)	-0.035(8)	0.069(5)	0.070(9)
C12	0.156(7)	0.150(6)	0.130(6)	-0.004(5)	0.105(5)	0.039(4)
C13	0.101(4)	0.104(3)	0.087(3)	0.028(3)	0.056(3)	0.046(3)

The general temperature factor expression: $\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl))$

Table S1-4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Br1	Mn1	2.5711(9)	Br1	Mn1 ¹	2.5905(10)
Mn1	Si1	2.5205(11)	Mn1	O1	2.116(3)
Si1	Si2	2.3332(15)	Si1	Si3	2.3332(12)
Si1	Si4	2.3365(13)	Si2	C1	1.870(5)
Si2	C2	1.877(5)	Si2	C3	1.871(4)
Si3	C4	1.861(5)	Si3	C5	1.868(5)
Si3	C6	1.873(5)	Si4	C7	1.871(6)
Si4	C8	1.877(4)	Si4	C9	1.872(5)
O1	C10	1.448(5)	O1	C13	1.416(6)
C10	C11	1.439(12)	C11	C12	1.386(11)
C12	C13	1.487(11)			

Symmetry Operators:

(1) -X+1,-Y,-Z+1

Table S1-5. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
Mn1	Br1	Mn1 ¹	83.841(19)	Br1	Mn1	Br1 ¹	96.159(19)
Br1	Mn1	Si1	122.00(3)	Br1	Mn1	O1	99.50(7)
Br1 ¹	Mn1	Si1	118.73(2)	Br1 ¹	Mn1	O1	96.54(8)
Si1	Mn1	O1	118.65(7)	Mn1	Si1	Si2	108.46(3)
Mn1	Si1	Si3	109.31(4)	Mn1	Si1	Si4	112.85(4)
Si2	Si1	Si3	109.17(5)	Si2	Si1	Si4	107.82(5)
Si3	Si1	Si4	109.16(4)	Si1	Si2	C1	114.21(15)
Si1	Si2	C2	109.52(18)	Si1	Si2	C3	110.70(16)
C1	Si2	C2	108.2(2)	C1	Si2	C3	107.1(2)
C2	Si2	C3	106.85(19)	Si1	Si3	C4	110.88(14)
Si1	Si3	C5	113.45(19)	Si1	Si3	C6	108.94(17)
C4	Si3	C5	107.3(2)	C4	Si3	C6	107.2(2)

C5	Si3	C6	108.9(2)	Si1	Si4	C7	114.12(18)
Si1	Si4	C8	110.91(16)	Si1	Si4	C9	109.56(14)
C7	Si4	C8	107.1(2)	C7	Si4	C9	107.9(2)
C8	Si4	C9	107.0(3)	Mn1	O1	C10	121.3(3)
Mn1	O1	C13	128.2(3)	C10	O1	C13	110.1(4)
O1	C10	C11	105.0(5)	C10	C11	C12	111.3(7)
C11	C12	C13	107.1(7)	O1	C13	C12	106.2(4)

Symmetry Operators:

(1) -X+1,-Y,-Z+1

Table S1-6. Torsion Angles(°)

(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
Mn1	Br1	Mn1 ¹	Br1 ¹	-0.000(17)	Mn1	Br1	Mn1 ¹	Si1 ¹	-131.84(3)
Mn1	Br1	Mn1 ¹	O1 ¹	100.34(3)	Mn1 ¹	Br1	Mn1	Br1 ¹	0.000(16)
Mn1 ¹	Br1	Mn1	Si1	-129.61(2)	Mn1 ¹	Br1	Mn1	O1	97.72(2)
Br1	Mn1	Si1	Si2	14.26(4)	Br1	Mn1	Si1	Si3	133.19(3)
Br1	Mn1	Si1	Si4	-105.14(4)	Br1	Mn1	O1	C10	-160.64(16)
Br1	Mn1	O1	C13	12.1(2)	Br1 ¹	Mn1	Si1	Si2	-104.88(3)
Br1 ¹	Mn1	Si1	Si3	14.06(4)	Br1 ¹	Mn1	Si1	Si4	135.73(3)
Br1 ¹	Mn1	O1	C10	-63.24(17)	Br1 ¹	Mn1	O1	C13	109.5(2)
Si1	Mn1	O1	C10	64.6(2)	Si1	Mn1	O1	C13	-122.67(18)
O1	Mn1	Si1	Si2	138.54(9)	O1	Mn1	Si1	Si3	-102.52(9)
O1	Mn1	Si1	Si4	19.15(9)	Mn1	Si1	Si2	C1	166.75(4)
Mn1	Si1	Si2	C2	-71.73(5)	Mn1	Si1	Si2	C3	45.84(5)
Mn1	Si1	Si3	C4	-66.38(6)	Mn1	Si1	Si3	C5	172.84(4)
Mn1	Si1	Si3	C6	51.35(5)	Mn1	Si1	Si4	C7	158.30(4)
Mn1	Si1	Si4	C8	-80.68(5)	Mn1	Si1	Si4	C9	37.21(6)
Si2	Si1	Si3	C4	52.11(6)	Si2	Si1	Si3	C5	-68.67(6)
Si2	Si1	Si3	C6	169.84(4)	Si3	Si1	Si2	C1	47.73(6)
Si3	Si1	Si2	C2	169.25(4)	Si3	Si1	Si2	C3	-73.18(5)
Si2	Si1	Si4	C7	38.54(5)	Si2	Si1	Si4	C8	159.56(4)
Si2	Si1	Si4	C9	-82.55(6)	Si4	Si1	Si2	C1	-70.75(5)
Si4	Si1	Si2	C2	50.78(5)	Si4	Si1	Si2	C3	168.35(4)
Si3	Si1	Si4	C7	-79.94(6)	Si3	Si1	Si4	C8	41.07(6)
Si3	Si1	Si4	C9	158.97(5)	Si4	Si1	Si3	C4	169.74(5)
Si4	Si1	Si3	C5	48.97(7)	Si4	Si1	Si3	C6	-72.53(6)
Mn1	O1	C10	C11	178.7(2)	Mn1	O1	C13	C12	-175.91(19)
C10	O1	C13	C12	-2.6(5)	C13	O1	C10	C11	4.8(6)

O1	C10	C11	C12	-5.4(11)	C10	C11	C12	C13	4.0(11)
C11	C12	C13	O1	-0.8(9)					

Symmetry Operators:

(1) $-X+1,-Y,-Z+1$

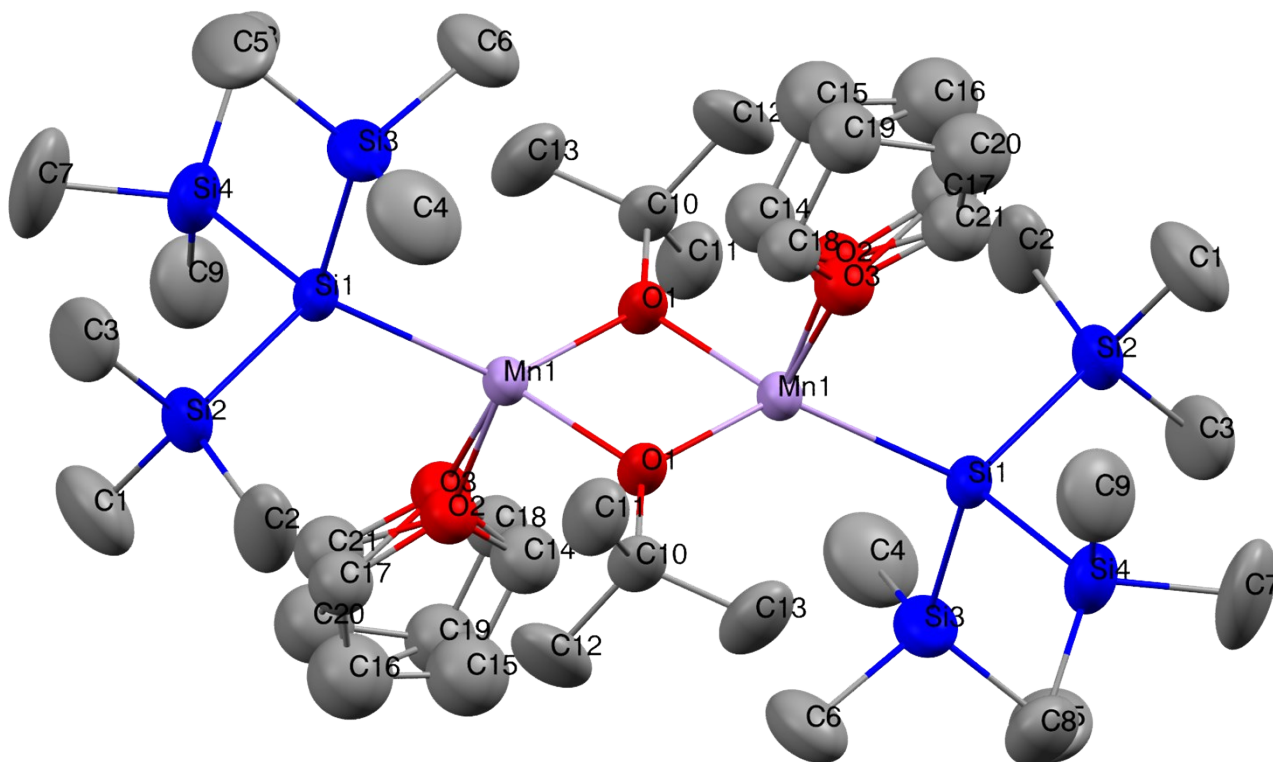


Figure S8. ORTEP drawing of **3** (50% probability of the thermal ellipsoids). The site occupancy factor for the oxygen and carbon atoms derived from the coordinated THF moieties were defined as 0.5. For details, the site occupancy factor was defined as follows: 0.5 for O2, O3, C14, C15, C16, C17, C18, C19, C20 and C21, respectively.

Table S2-1. Crystal data and structure refinement for **3**.

Empirical Formula	C ₃₄ H ₈₈ Mn ₂ O ₄ Si ₈
Formula Weight	895.63
Crystal Color, Habit	colorless, platelet
Crystal Dimensions	0.100 X 0.050 X 0.020 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 9.820(4) Å b = 9.922(4) Å c = 14.623(5) Å α = 97.082(5) ° β = 98.990(4) ° γ = 100.713(6) ° V = 1365.6(9) Å ³
Space Group	P-1 (#2)
Z value	1
D _{calc}	1.089 g/cm ³
F ₀₀₀	486.00
μ(MoKα)	6.657 cm ⁻¹
Diffractometer	Saturn724
Radiation	MoKα (λ = 0.71075 Å) multi-layer mirror monochromated
Voltage, Current	50kV, 24mA
Temperature	-30.0°C
Detector Aperture	72.8 x 72.8 mm
Data Images	2880 exposures
ω oscillation Range (χ=45.0, φ=0.0)	-70.0 - 110.0°
Exposure Rate	64.0 sec./°
Detector Swing Angle	19.88°
ω oscillation Range (χ=45.0, φ=90.0)	-70.0 - 110.0°
Exposure Rate	64.0 sec./°
Detector Swing Angle	19.88°
ω oscillation Range (χ=45.0, φ=180.0)	-70.0 - 110.0°
Exposure Rate	64.0 sec./°
Detector Swing Angle	19.88°
ω oscillation Range (χ=45.0, φ=270.0)	-70.0 - 110.0°
Exposure Rate	64.0 sec./°
Detector Swing Angle	19.88°
Detector Position	44.64 mm

Pixel Size	0.141 mm
$2\theta_{\max}$	54.9°
No. of Reflections Measured	Total: 21717 Unique: 6162 ($R_{\text{int}} = 0.1579$)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.844 - 0.987)
Structure Solution	Direct Methods (SHELXT Version 2014/5)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1 / [\sigma^2(F_o^2) + (0.0525 \cdot P)^2 + 3.1899 \cdot P]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$
$2\theta_{\max}$ cutoff	54.9°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	6162
No. Variables	212
Reflection/Parameter Ratio	29.07
Residuals: R1 ($I > 2.00\sigma(I)$)	0.0772
Residuals: R (All reflections)	0.0826
Residuals: wR2 (All reflections)	0.2153
Goodness of Fit Indicator	1.073
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.73 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.66 e ⁻ /Å ³

Table S2-2. Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$

atom	x	y	z	B_{eq}	occ
Mn1	0.45665(6)	0.46433(6)	0.39015(4)	2.739(14)	1
Si1	0.31154(11)	0.30228(11)	0.24009(7)	2.89(2)	1
Si2	0.43094(15)	0.19268(16)	0.13450(9)	4.43(3)	1
Si3	0.15916(15)	0.11559(14)	0.27845(11)	4.36(3)	1
Si4	0.16035(16)	0.40831(16)	0.14413(9)	4.60(3)	1
O1	0.4010(3)	0.5720(3)	0.50178(19)	3.20(5)	1
O2	0.5950(8)	0.6276(8)	0.3418(6)	3.69(15)	1/2
O3	0.5635(9)	0.6486(9)	0.3356(6)	4.06(17)	1/2
C1	0.5097(10)	0.3105(9)	0.0584(6)	8.6(2)	1
C2	0.5829(8)	0.1275(9)	0.1951(5)	7.7(2)	1
C3	0.3151(8)	0.0386(7)	0.0542(5)	7.17(17)	1
C4	0.2579(10)	-0.0160(7)	0.3212(7)	8.1(2)	1
C5	0.0125(8)	0.0198(9)	0.1802(6)	8.8(2)	1
C6	0.0689(8)	0.1741(7)	0.3759(5)	6.93(16)	1
C7	0.1055(10)	0.3161(10)	0.0203(5)	9.3(3)	1
C8	-0.0076(6)	0.4190(8)	0.1867(5)	6.58(15)	1
C9	0.2508(8)	0.5928(7)	0.1381(5)	7.30(17)	1
C10	0.2875(5)	0.6420(5)	0.5078(3)	3.86(8)	1
C11	0.3476(7)	0.7957(6)	0.5395(4)	5.64(12)	1
C12	0.2034(7)	0.5817(8)	0.5784(5)	6.64(16)	1
C13	0.1935(6)	0.6170(7)	0.4131(5)	6.03(14)	1
C14	0.6609(15)	0.7675(14)	0.4015(10)	5.5(3)	1/2
C15	0.781(2)	0.8167(19)	0.3529(14)	7.8(4)	1/2
C16	0.756(2)	0.7367(19)	0.2587(14)	8.3(4)	1/2
C17	0.6473(14)	0.6081(13)	0.2535(9)	4.7(2)	1/2
C18	0.6142(13)	0.7811(12)	0.3790(8)	4.40(19)	1/2
C19	0.7313(15)	0.8456(14)	0.3316(10)	5.8(3)	1/2
C20	0.6831(18)	0.7591(17)	0.2310(12)	7.2(3)	1/2
C21	0.6053(15)	0.6323(14)	0.2446(10)	5.4(3)	1/2

$$B_{\text{eq}} = \frac{8}{3} \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos \gamma + 2U_{13}(aa^*cc^*)\cos \beta + 2U_{23}(bb^*cc^*)\cos \alpha)$$

Table S2-3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn1	0.0349(3)	0.0376(3)	0.0302(3)	0.0065(2)	0.0056(2)	0.0021(2)
Si1	0.0388(5)	0.0392(5)	0.0297(5)	0.0086(4)	0.0032(4)	0.0001(4)
Si2	0.0611(8)	0.0709(9)	0.0371(6)	0.0217(7)	0.0131(6)	-0.0057(6)
Si3	0.0585(8)	0.0435(7)	0.0584(8)	-0.0019(6)	0.0152(6)	0.0013(6)

Si4	0.0639(8)	0.0709(9)	0.0408(7)	0.0273(7)	-0.0033(6)	0.0089(6)
O1	0.0374(13)	0.0499(16)	0.0351(14)	0.0201(12)	0.0022(11)	-0.0010(12)
C1	0.134(7)	0.116(6)	0.085(5)	0.021(5)	0.062(5)	0.009(5)
C2	0.106(5)	0.144(7)	0.056(3)	0.078(5)	0.013(3)	-0.010(4)
C3	0.103(5)	0.090(5)	0.069(4)	0.020(4)	0.021(4)	-0.033(3)
C4	0.139(7)	0.064(4)	0.126(7)	0.031(4)	0.047(6)	0.045(4)
C5	0.083(5)	0.112(6)	0.101(6)	-0.046(4)	0.015(4)	-0.027(5)
C6	0.092(5)	0.081(4)	0.094(5)	0.004(4)	0.049(4)	0.006(4)
C7	0.146(7)	0.150(8)	0.055(4)	0.081(6)	-0.032(4)	-0.008(4)
C8	0.060(3)	0.110(5)	0.079(4)	0.031(3)	-0.006(3)	0.013(4)
C9	0.120(6)	0.082(4)	0.088(5)	0.040(4)	0.012(4)	0.041(4)
C10	0.043(2)	0.057(3)	0.050(2)	0.0255(19)	0.0061(18)	-0.002(2)
C11	0.079(4)	0.067(3)	0.065(3)	0.031(3)	0.000(3)	-0.010(3)
C12	0.070(4)	0.117(5)	0.091(5)	0.049(4)	0.045(3)	0.032(4)
C13	0.061(3)	0.080(4)	0.081(4)	0.037(3)	-0.017(3)	-0.008(3)

The general temperature factor expression: $\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl))$

Table S2-4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Mn1	Si1	2.5946(12)	Mn1	O1	2.042(3)
Mn1	O1 ¹	2.054(3)	Mn1	O2	2.177(8)
Mn1	O3	2.233(9)	Si1	Si2	2.359(2)
Si1	Si3	2.3394(19)	Si1	Si4	2.361(2)
Si2	C1	1.860(9)	Si2	C2	1.875(8)
Si2	C3	1.872(6)	Si3	C4	1.876(9)
Si3	C5	1.884(7)	Si3	C6	1.880(8)
Si4	C7	1.873(7)	Si4	C8	1.867(7)
Si4	C9	1.899(7)	O1	C10	1.426(6)
O2	O3	0.409(13)	O2	C14	1.516(14)
O2	C17	1.466(16)	O2	C18	1.519(14)
O2	C21	1.445(17)	O3	C14	1.499(14)
O3	C17	1.611(17)	O3	C18	1.353(13)
O3	C21	1.452(18)	C10	C11	1.515(7)
C10	C12	1.528(9)	C10	C13	1.505(7)
C14	C15	1.51(3)	C14	C18	0.569(19)
C14	C19	1.53(2)	C15	C16	1.46(3)
C15	C18	1.73(2)	C15	C19	0.67(3)
C15	C20	1.85(2)	C16	C17	1.49(2)
C16	C19	1.50(2)	C16	C20	0.84(3)

C16	C21	1.61(2)	C17	C20	1.56(2)
C17	C21	0.52(2)	C18	C19	1.52(2)
C19	C20	1.56(2)	C20	C21	1.40(2)

Symmetry Operators:

(1) -X+1,-Y+1,-Z+1

Table S2-5. Bond angles ($^{\circ}$)

atom	atom	atom	angle	atom	atom	atom	angle
Si1	Mn1	O1	132.98(8)	Si1	Mn1	O1 ¹	131.21(9)
Si1	Mn1	O2	105.9(2)	Si1	Mn1	O3	103.7(2)
O1	Mn1	O1 ¹	79.58(12)	O1	Mn1	O2	101.8(2)
O1	Mn1	O3	96.8(2)	O1 ¹	Mn1	O2	98.5(2)
O1 ¹	Mn1	O3	106.9(2)	O2	Mn1	O3	10.6(3)
Mn1	Si1	Si2	119.20(6)	Mn1	Si1	Si3	110.88(6)
Mn1	Si1	Si4	114.32(6)	Si2	Si1	Si3	103.05(7)
Si2	Si1	Si4	103.88(7)	Si3	Si1	Si4	103.87(7)
Si1	Si2	C1	113.1(3)	Si1	Si2	C2	112.9(2)
Si1	Si2	C3	113.2(3)	C1	Si2	C2	104.7(4)
C1	Si2	C3	106.5(3)	C2	Si2	C3	105.8(3)
Si1	Si3	C4	111.1(3)	Si1	Si3	C5	115.2(3)
Si1	Si3	C6	111.4(2)	C4	Si3	C5	107.0(4)
C4	Si3	C6	106.3(4)	C5	Si3	C6	105.3(3)
Si1	Si4	C7	113.6(3)	Si1	Si4	C8	113.5(2)
Si1	Si4	C9	110.4(2)	C7	Si4	C8	105.4(4)
C7	Si4	C9	106.6(4)	C8	Si4	C9	106.9(4)
Mn1	O1	Mn1 ¹	100.42(14)	Mn1	O1	C10	131.4(2)
Mn1 ¹	O1	C10	127.9(3)	Mn1	O2	O3	92.6(17)
Mn1	O2	C14	123.0(8)	Mn1	O2	C17	123.5(6)
Mn1	O2	C18	123.5(7)	Mn1	O2	C21	124.4(6)
O3	O2	C14	79.9(15)	O3	O2	C17	103.4(19)
O3	O2	C18	58.8(14)	O3	O2	C21	82.8(18)
C14	O2	C17	113.1(9)	C14	O2	C18	21.6(7)
C14	O2	C21	110.7(9)	C17	O2	C18	110.8(9)
C17	O2	C21	20.6(8)	C18	O2	C21	101.0(9)
Mn1	O3	O2	76.8(16)	Mn1	O3	C14	120.4(8)
Mn1	O3	C17	113.2(6)	Mn1	O3	C18	129.9(8)
Mn1	O3	C21	120.4(7)	O2	O3	C14	84.5(15)
O2	O3	C17	62.3(17)	O2	O3	C18	106.2(16)
O2	O3	C21	81.0(18)	C14	O3	C17	106.2(9)

C14	O3	C18	22.3(8)	C14	O3	C21	111.3(9)
C17	O3	C18	111.7(9)	C17	O3	C21	18.7(8)
C18	O3	C21	109.2(10)	O1	C10	C11	108.8(4)
O1	C10	C12	108.4(5)	O1	C10	C13	108.9(4)
C11	C10	C12	110.7(5)	C11	C10	C13	110.7(5)
C12	C10	C13	109.3(4)	O2	C14	O3	15.6(5)
O2	C14	C15	101.0(12)	O2	C14	C18	79.6(16)
O2	C14	C19	101.4(10)	O3	C14	C15	106.7(12)
O3	C14	C18	64.3(16)	O3	C14	C19	100.2(10)
C15	C14	C18	103(2)	C15	C14	C19	25.4(10)
C18	C14	C19	78(2)	C14	C15	C16	109.3(14)
C14	C15	C18	18.7(7)	C14	C15	C19	79(2)
C14	C15	C20	96.9(11)	C16	C15	C18	100.2(12)
C16	C15	C19	80(2)	C16	C15	C20	26.2(10)
C18	C15	C19	61(2)	C18	C15	C20	82.5(10)
C19	C15	C20	54.4(19)	C15	C16	C17	109.2(16)
C15	C16	C19	26.1(10)	C15	C16	C20	104(2)
C15	C16	C21	107.1(16)	C17	C16	C19	108.2(15)
C17	C16	C20	78.9(17)	C17	C16	C21	18.9(8)
C19	C16	C20	78.1(19)	C19	C16	C21	97.9(14)
C20	C16	C21	60.6(16)	O2	C17	O3	14.3(5)
O2	C17	C16	104.1(11)	O2	C17	C20	102.9(11)
O2	C17	C21	77(2)	O3	C17	C16	103.0(11)
O3	C17	C20	94.4(10)	O3	C17	C21	63(2)
C16	C17	C20	32.0(10)	C16	C17	C21	93(2)
C20	C17	C21	62(2)	O2	C18	O3	15.0(5)
O2	C18	C14	78.8(18)	O2	C18	C15	91.7(10)
O2	C18	C19	101.9(10)	O3	C18	C14	93.4(19)
O3	C18	C15	102.5(10)	O3	C18	C19	108.0(10)
C14	C18	C15	58(2)	C14	C18	C19	81(2)
C15	C18	C19	22.6(9)	C14	C19	C15	76(2)
C14	C19	C16	106.2(13)	C14	C19	C18	21.5(7)
C14	C19	C20	109.7(11)	C15	C19	C16	74(2)
C15	C19	C18	97(2)	C15	C19	C20	105(2)
C16	C19	C18	108.8(12)	C16	C19	C20	31.9(10)
C18	C19	C20	100.3(10)	C15	C20	C16	50.0(17)
C15	C20	C17	89.0(11)	C15	C20	C19	20.4(9)
C15	C20	C21	97.8(13)	C16	C20	C17	69.1(17)
C16	C20	C19	70.0(18)	C16	C20	C21	88(2)

C17	C20	C19	101.5(13)	C17	C20	C21	19.3(8)
C19	C20	C21	104.5(14)	O2	C21	O3	16.2(5)
O2	C21	C16	99.4(11)	O2	C21	C17	82(2)
O2	C21	C20	112.7(11)	O3	C21	C16	104.9(11)
O3	C21	C17	98(2)	O3	C21	C20	109.4(12)
C16	C21	C17	68(2)	C16	C21	C20	31.7(11)
C17	C21	C20	98(2)				

Symmetry Operators:

(1) -X+1,-Y+1,-Z+1

Table S2-6. Torsion Angles(^o)

(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
Si1	Mn1	O1	Mn1 ¹	138.09(7)	Si1	Mn1	O1	C10	-36.1(3)
O1	Mn1	Si1	Si2	-176.87(12)	O1	Mn1	Si1	Si3	-57.53(14)
O1	Mn1	Si1	Si4	59.48(14)	Si1	Mn1	O1 ¹	Mn1 ¹	-139.49(8)
Si1	Mn1	O1 ¹	C10 ¹	46.1(3)	O1 ¹	Mn1	Si1	Si2	-57.70(13)
O1 ¹	Mn1	Si1	Si3	61.64(13)	O1 ¹	Mn1	Si1	Si4	178.64(11)
Si1	Mn1	O2	O3	79.1(11)	Si1	Mn1	O2	C14	158.8(5)
Si1	Mn1	O2	C17	-28.8(6)	Si1	Mn1	O2	C18	132.9(4)
Si1	Mn1	O2	C21	-3.9(7)	O2	Mn1	Si1	Si2	59.3(2)
O2	Mn1	Si1	Si3	178.6(2)	O2	Mn1	Si1	Si4	-64.4(2)
Si1	Mn1	O3	O2	-103.6(11)	Si1	Mn1	O3	C14	-179.1(5)
Si1	Mn1	O3	C17	-51.9(4)	Si1	Mn1	O3	C18	156.2(6)
Si1	Mn1	O3	C21	-32.5(6)	O3	Mn1	Si1	Si2	69.9(3)
O3	Mn1	Si1	Si3	-170.7(3)	O3	Mn1	Si1	Si4	-53.7(3)
O1	Mn1	O1 ¹	Mn1 ¹	-0.00(11)	O1	Mn1	O1 ¹	C10 ¹	-174.5(2)
O1 ¹	Mn1	O1	Mn1 ¹	0.00(11)	O1 ¹	Mn1	O1	C10	-174.2(2)
O1	Mn1	O2	O3	-62.5(11)	O1	Mn1	O2	C14	17.1(6)
O1	Mn1	O2	C17	-170.5(5)	O1	Mn1	O2	C18	-8.8(5)
O1	Mn1	O2	C21	-145.6(6)	O2	Mn1	O1	Mn1 ¹	-96.6(2)
O2	Mn1	O1	C10	89.2(3)	O1	Mn1	O3	O2	119.0(11)
O1	Mn1	O3	C14	43.6(6)	O1	Mn1	O3	C17	170.7(4)
O1	Mn1	O3	C18	18.8(7)	O1	Mn1	O3	C21	-169.9(5)
O3	Mn1	O1	Mn1 ¹	-106.0(2)	O3	Mn1	O1	C10	79.8(3)
O1 ¹	Mn1	O2	O3	-143.5(10)	O1 ¹	Mn1	O2	C14	-63.9(6)
O1 ¹	Mn1	O2	C17	108.5(5)	O1 ¹	Mn1	O2	C18	-89.8(5)
O1 ¹	Mn1	O2	C21	133.4(6)	O2	Mn1	O1 ¹	Mn1 ¹	100.6(2)
O2	Mn1	O1 ¹	C10 ¹	-73.9(3)	O1 ¹	Mn1	O3	O2	37.9(12)

O1 ¹	Mn1	O3	C14	-37.6(6)	O1 ¹	Mn1	O3	C17	89.6(4)
O1 ¹	Mn1	O3	C18	-62.4(7)	O1 ¹	Mn1	O3	C21	109.0(5)
O3	Mn1	O1 ¹	Mn1 ¹	94.0(3)	O3	Mn1	O1 ¹	C10 ¹	-80.4(3)
Mn1	Si1	Si2	C1	-77.98(8)	Mn1	Si1	Si2	C2	40.64(10)
Mn1	Si1	Si2	C3	160.82(6)	Mn1	Si1	Si3	C4	-75.05(8)
Mn1	Si1	Si3	C5	163.09(6)	Mn1	Si1	Si3	C6	43.32(9)
Mn1	Si1	Si4	C7	159.95(6)	Mn1	Si1	Si4	C8	-79.73(8)
Mn1	Si1	Si4	C9	40.26(9)	Si2	Si1	Si3	C4	53.59(9)
Si2	Si1	Si3	C5	-68.28(9)	Si2	Si1	Si3	C6	171.96(7)
Si3	Si1	Si2	C1	158.75(7)	Si3	Si1	Si2	C2	-82.63(8)
Si3	Si1	Si2	C3	37.54(9)	Si2	Si1	Si4	C7	28.41(9)
Si2	Si1	Si4	C8	148.73(7)	Si2	Si1	Si4	C9	-91.28(8)
Si4	Si1	Si2	C1	50.64(8)	Si4	Si1	Si2	C2	169.26(7)
Si4	Si1	Si2	C3	-70.56(9)	Si3	Si1	Si4	C7	-79.09(9)
Si3	Si1	Si4	C8	41.24(9)	Si3	Si1	Si4	C9	161.23(7)
Si4	Si1	Si3	C4	161.70(7)	Si4	Si1	Si3	C5	39.84(10)
Si4	Si1	Si3	C6	-79.93(8)	Mn1	O1	C10	C11	-115.9(3)
Mn1	O1	C10	C12	123.6(3)	Mn1	O1	C10	C13	4.8(5)
Mn1 ¹	O1	C10	C11	71.3(4)	Mn1 ¹	O1	C10	C12	-49.1(4)
Mn1 ¹	O1	C10	C13	-167.90(19)	Mn1	O2	O3	Mn1	0.000(14)
Mn1	O2	O3	C14	123.0(4)	Mn1	O2	O3	C17	-125.4(7)
Mn1	O2	O3	C18	128.2(8)	Mn1	O2	O3	C21	-124.3(4)
Mn1	O2	C14	C15	160.3(6)	Mn1	O2	C14	C18	-98.5(15)
Mn1	O2	C14	C19	-173.7(5)	Mn1	O2	C17	C16	-170.2(5)
Mn1	O2	C17	C20	156.8(5)	Mn1	O2	C17	C21	99.3(13)
Mn1	O2	C18	C14	95.8(13)	Mn1	O2	C18	C15	153.2(5)
Mn1	O2	C18	C19	173.7(5)	Mn1	O2	C21	C16	-160.3(5)
Mn1	O2	C21	C17	-94.7(15)	Mn1	O2	C21	C20	169.7(7)
O3	O2	C14	C15	-113.1(19)	O3	O2	C14	C18	-12(2)
O3	O2	C14	C19	-87.2(19)	C14	O2	O3	Mn1	-123.0(7)
C14	O2	O3	C14	0.0(6)	C14	O2	O3	C17	111.6(9)
C14	O2	O3	C18	5.1(9)	C14	O2	O3	C21	112.6(7)
O3	O2	C17	C16	87.4(17)	O3	O2	C17	C20	54.4(17)
O3	O2	C17	C21	-3(2)	C17	O2	O3	Mn1	125.4(8)
C17	O2	O3	C14	-111.6(8)	C17	O2	O3	C17	-0.0(5)
C17	O2	O3	C18	-106.4(10)	C17	O2	O3	C21	1.1(7)
O3	O2	C18	C14	166(2)	O3	O2	C18	C15	-136(2)
O3	O2	C18	C19	-116(2)	C18	O2	O3	Mn1	-128.2(10)
C18	O2	O3	C14	-5.1(9)	C18	O2	O3	C17	106.4(10)

C18	O2	O3	C18	0.0(6)	C18	O2	O3	C21	107.5(11)
O3	O2	C21	C16	111.4(16)	O3	O2	C21	C17	177(2)
O3	O2	C21	C20	81.4(17)	C21	O2	O3	Mn1	124.3(6)
C21	O2	O3	C14	-112.6(6)	C21	O2	O3	C17	-1.1(7)
C21	O2	O3	C18	-107.5(10)	C21	O2	O3	C21	0.0(5)
C14	O2	C17	C16	2.8(12)	C14	O2	C17	C20	-30.1(11)
C14	O2	C17	C21	-87.6(14)	C17	O2	C14	C15	-12.8(12)
C17	O2	C14	C18	88.4(17)	C17	O2	C14	C19	13.2(12)
C14	O2	C18	C14	-0.0(16)	C14	O2	C18	C15	57.4(19)
C14	O2	C18	C19	78(2)	C18	O2	C14	C15	-101(2)
C18	O2	C14	C18	-0.0(13)	C18	O2	C14	C19	-75(2)
C14	O2	C21	C16	35.2(12)	C14	O2	C21	C17	100.8(16)
C14	O2	C21	C20	5.1(15)	C21	O2	C14	C15	-34.9(12)
C21	O2	C14	C18	66.2(18)	C21	O2	C14	C19	-8.9(13)
C17	O2	C18	C14	-100.4(14)	C17	O2	C18	C15	-43.0(9)
C17	O2	C18	C19	-22.6(10)	C18	O2	C17	C16	26.0(11)
C18	O2	C17	C20	-6.9(10)	C18	O2	C17	C21	-64.4(14)
C17	O2	C21	C16	-65.6(18)	C17	O2	C21	C17	0.0(13)
C17	O2	C21	C20	-96(2)	C21	O2	C17	C16	90(2)
C21	O2	C17	C20	57.5(18)	C21	O2	C17	C21	0.0(14)
C18	O2	C21	C16	55.2(10)	C18	O2	C21	C17	120.8(14)
C18	O2	C21	C20	25.2(13)	C21	O2	C18	C14	-119.3(14)
C21	O2	C18	C15	-61.9(8)	C21	O2	C18	C19	-41.5(10)
Mn1	O3	C14	C15	141.7(7)	Mn1	O3	C14	C18	-121.9(14)
Mn1	O3	C14	C19	167.0(6)	Mn1	O3	C17	C16	-155.7(6)
Mn1	O3	C17	C20	173.0(4)	Mn1	O3	C17	C21	117.0(12)
Mn1	O3	C18	C14	72.6(17)	Mn1	O3	C18	C15	131.1(7)
Mn1	O3	C18	C19	153.9(6)	Mn1	O3	C21	C16	-140.7(6)
Mn1	O3	C21	C17	-71.8(16)	Mn1	O3	C21	C20	-173.6(6)
O2	O3	C14	C15	70.5(19)	O2	O3	C14	C18	167(2)
O2	O3	C14	C19	95.8(19)	O2	O3	C17	C16	-96.1(17)
O2	O3	C17	C20	-127.3(16)	O2	O3	C17	C21	177(2)
O2	O3	C18	C14	-14(2)	O2	O3	C18	C15	45(2)
O2	O3	C18	C19	68(2)	O2	O3	C21	C16	-71.9(16)
O2	O3	C21	C17	-3(2)	O2	O3	C21	C20	-104.8(17)
C14	O3	C17	C16	-21.4(11)	C14	O3	C17	C20	-52.7(10)
C14	O3	C17	C21	-108.7(14)	C17	O3	C14	C15	11.4(12)
C17	O3	C14	C18	107.9(16)	C17	O3	C14	C19	36.8(11)
C14	O3	C18	C14	-0.0(16)	C14	O3	C18	C15	58(2)

C14	O3	C18	C19	81(2)	C18	O3	C14	C15	-96(2)
C18	O3	C14	C18	0.0(15)	C18	O3	C14	C19	-71(2)
C14	O3	C21	C16	8.6(13)	C14	O3	C21	C17	77.5(18)
C14	O3	C21	C20	-24.3(14)	C21	O3	C14	C15	-7.6(14)
C21	O3	C14	C18	88.8(17)	C21	O3	C14	C19	17.7(13)
C17	O3	C18	C14	-79.7(16)	C17	O3	C18	C15	-21.2(11)
C17	O3	C18	C19	1.6(12)	C18	O3	C17	C16	1.4(12)
C18	O3	C17	C20	-29.8(10)	C18	O3	C17	C21	-85.8(14)
C18	O3	C21	C16	32.2(12)	C18	O3	C21	C17	101.1(17)
C18	O3	C21	C20	-0.6(14)	C21	O3	C18	C14	-99.5(15)
C21	O3	C18	C15	-41.0(11)	C21	O3	C18	C19	-18.2(12)
O2	C14	C15	C16	18.0(16)	O2	C14	C15	C19	93.4(16)
O2	C14	C15	C20	41.8(12)	O2	C14	C18	O2	-0.0(3)
O2	C14	C18	O3	3.6(7)	O2	C14	C18	C15	-99.0(10)
O2	C14	C18	C19	-104.2(7)	O2	C14	C19	C15	-91.7(13)
O2	C14	C19	C16	-23.8(12)	O2	C14	C19	C18	76.6(12)
O2	C14	C19	C20	9.6(13)	O3	C14	C15	C16	3.0(17)
O3	C14	C15	C19	78.4(17)	O3	C14	C15	C20	26.9(13)
O3	C14	C18	O2	-3.6(7)	O3	C14	C18	O3	0.0(4)
O3	C14	C18	C15	-102.6(11)	O3	C14	C18	C19	-107.7(9)
O3	C14	C19	C15	-107.6(13)	O3	C14	C19	C16	-39.6(12)
O3	C14	C19	C18	60.7(11)	O3	C14	C19	C20	-6.2(14)
C15	C14	C18	O2	99.0(12)	C15	C14	C18	O3	102.6(12)
C15	C14	C18	C15	0.0(7)	C15	C14	C18	C19	-5.1(10)
C18	C14	C15	C16	-64(2)	C18	C14	C15	C19	12(2)
C18	C14	C15	C20	-40(2)	C15	C14	C19	C15	-0.0(15)
C15	C14	C19	C16	67.9(19)	C15	C14	C19	C18	168(2)
C15	C14	C19	C20	101(2)	C19	C14	C15	C16	-75.4(19)
C19	C14	C15	C19	-0.0(11)	C19	C14	C15	C20	-51.6(16)
C18	C14	C19	C15	-168(2)	C18	C14	C19	C16	-100.3(19)
C18	C14	C19	C18	-0.0(11)	C18	C14	C19	C20	-67.0(19)
C19	C14	C18	O2	104.2(8)	C19	C14	C18	O3	107.7(9)
C19	C14	C18	C15	5.1(9)	C19	C14	C18	C19	-0.0(5)
C14	C15	C16	C17	-18(2)	C14	C15	C16	C19	74.5(17)
C14	C15	C16	C20	65(2)	C14	C15	C16	C21	2(2)
C14	C15	C19	C14	-0.0(5)	C14	C15	C19	C16	-112.0(9)
C14	C15	C19	C18	-4.3(9)	C14	C15	C19	C20	-106.9(12)
C14	C15	C20	C16	-120.4(17)	C14	C15	C20	C17	-57.3(12)
C14	C15	C20	C19	71.1(18)	C14	C15	C20	C21	-40.0(14)

C16	C15	C18	O2	45.0(14)	C16	C15	C18	O3	34.4(15)
C16	C15	C18	C14	120.7(18)	C16	C15	C18	C19	-72.5(17)
C18	C15	C16	C17	-34.8(17)	C18	C15	C16	C19	57.5(14)
C18	C15	C16	C20	48(2)	C18	C15	C16	C21	-15.0(17)
C16	C15	C19	C14	112.0(11)	C16	C15	C19	C16	0.0(8)
C16	C15	C19	C18	107.7(11)	C16	C15	C19	C20	5.1(14)
C19	C15	C16	C17	-92(2)	C19	C15	C16	C19	-0.0(13)
C19	C15	C16	C20	-9(3)	C19	C15	C16	C21	-72(2)
C16	C15	C20	C16	-0.0(17)	C16	C15	C20	C17	63(2)
C16	C15	C20	C19	-168(3)	C16	C15	C20	C21	80(2)
C20	C15	C16	C17	-83(2)	C20	C15	C16	C19	9(3)
C20	C15	C16	C20	-0.0(12)	C20	C15	C16	C21	-63.0(19)
C18	C15	C19	C14	4.3(8)	C18	C15	C19	C16	-107.7(9)
C18	C15	C19	C18	0.0(4)	C18	C15	C19	C20	-102.6(13)
C19	C15	C18	O2	117(2)	C19	C15	C18	O3	107(2)
C19	C15	C18	C14	-167(3)	C19	C15	C18	C19	-0.0(13)
C18	C15	C20	C16	-132.4(15)	C18	C15	C20	C17	-69.2(10)
C18	C15	C20	C19	59.1(15)	C18	C15	C20	C21	-52.0(11)
C20	C15	C18	O2	64.3(9)	C20	C15	C18	O3	53.8(10)
C20	C15	C18	C14	140.1(15)	C20	C15	C18	C19	-53.1(13)
C19	C15	C20	C16	168(3)	C19	C15	C20	C17	-128(2)
C19	C15	C20	C19	-0.0(16)	C19	C15	C20	C21	-111(2)
C20	C15	C19	C14	106.9(13)	C20	C15	C19	C16	-5.1(13)
C20	C15	C19	C18	102.6(14)	C20	C15	C19	C20	0.0(7)
C15	C16	C17	O2	9.0(18)	C15	C16	C17	O3	23.7(17)
C15	C16	C17	C20	101(2)	C15	C16	C17	C21	87(2)
C15	C16	C19	C14	-69(2)	C15	C16	C19	C15	0.0(17)
C15	C16	C19	C18	-92(2)	C15	C16	C19	C20	-171(3)
C15	C16	C20	C15	0.0(8)	C15	C16	C20	C17	-107.2(17)
C15	C16	C20	C19	4.2(11)	C15	C16	C20	C21	-102.1(15)
C15	C16	C21	O2	-22.1(17)	C15	C16	C21	O3	-6.5(18)
C15	C16	C21	C17	-99(2)	C15	C16	C21	C20	96.5(19)
C17	C16	C19	C14	27.4(16)	C17	C16	C19	C15	96.7(17)
C17	C16	C19	C18	5.0(17)	C17	C16	C19	C20	-73.9(14)
C19	C16	C17	O2	-18.5(16)	C19	C16	C17	O3	-3.8(16)
C19	C16	C17	C20	73.4(16)	C19	C16	C17	C21	59(2)
C17	C16	C20	C15	107.2(16)	C17	C16	C20	C17	0.0(5)
C17	C16	C20	C19	111.5(11)	C17	C16	C20	C21	5.1(8)
C20	C16	C17	O2	-91.9(19)	C20	C16	C17	O3	-77.2(19)

C20	C16	C17	C20	0.0(12)	C20	C16	C17	C21	-14(2)
C19	C16	C20	C15	-4.2(10)	C19	C16	C20	C17	-111.5(11)
C19	C16	C20	C19	0.0(6)	C19	C16	C20	C21	-106.3(11)
C20	C16	C19	C14	101.4(19)	C20	C16	C19	C15	171(2)
C20	C16	C19	C18	78.9(19)	C20	C16	C19	C20	-0.0(12)
C19	C16	C21	O2	-47.2(14)	C19	C16	C21	O3	-31.5(15)
C19	C16	C21	C17	-124.3(19)	C19	C16	C21	C20	71.4(14)
C21	C16	C19	C14	43.8(14)	C21	C16	C19	C15	113.0(16)
C21	C16	C19	C18	21.4(15)	C21	C16	C19	C20	-57.5(11)
C20	C16	C21	O2	-119(2)	C20	C16	C21	O3	-103(2)
C20	C16	C21	C17	164(3)	C20	C16	C21	C20	-0.0(14)
C21	C16	C20	C15	102.1(14)	C21	C16	C20	C17	-5.1(9)
C21	C16	C20	C19	106.3(11)	C21	C16	C20	C21	0.0(6)
O2	C17	C20	C15	49.0(9)	O2	C17	C20	C16	96.0(13)
O2	C17	C20	C19	32.8(12)	O2	C17	C21	O2	0.0(3)
O2	C17	C21	O3	0.8(6)	O2	C17	C21	C16	103.7(8)
O2	C17	C21	C20	112.0(10)	O3	C17	C20	C15	60.7(8)
O3	C17	C20	C16	107.6(12)	O3	C17	C20	C19	44.5(10)
O3	C17	C21	O2	-0.8(6)	O3	C17	C21	O3	-0.0(3)
O3	C17	C21	C16	102.8(10)	O3	C17	C21	C20	111.1(12)
C16	C17	C20	C15	-47.0(17)	C16	C17	C20	C16	0.0(15)
C16	C17	C20	C19	-63.2(18)	C16	C17	C21	O2	-103.7(11)
C16	C17	C21	O3	-102.8(12)	C16	C17	C21	C16	0.0(8)
C16	C17	C21	C20	8.3(14)	C20	C17	C21	O2	-112.0(12)
C20	C17	C21	O3	-111.1(14)	C20	C17	C21	C16	-8.3(14)
C20	C17	C21	C20	-0.0(7)	C21	C17	C20	C15	117(2)
C21	C17	C20	C16	164(3)	C21	C17	C20	C19	101(2)
O2	C18	C19	C14	-76.4(12)	O2	C18	C19	C15	-65.0(14)
O2	C18	C19	C16	10.1(12)	O2	C18	C19	C20	41.9(10)
O3	C18	C19	C14	-90.6(14)	O3	C18	C19	C15	-79.1(15)
O3	C18	C19	C16	-4.1(14)	O3	C18	C19	C20	27.7(12)
C14	C18	C19	C14	-0.0(14)	C14	C18	C19	C15	11(2)
C14	C18	C19	C16	86.5(19)	C14	C18	C19	C20	118.3(18)
C15	C18	C19	C14	-11(2)	C15	C18	C19	C15	-0.0(15)
C15	C18	C19	C16	75(2)	C15	C18	C19	C20	107(2)
C14	C19	C20	C15	-79.9(17)	C14	C19	C20	C16	-89.2(15)
C14	C19	C20	C17	-26.7(15)	C14	C19	C20	C21	-7.1(17)
C15	C19	C20	C15	0.0(17)	C15	C19	C20	C16	-9(2)
C15	C19	C20	C17	53(2)	C15	C19	C20	C21	73(3)

C16	C19	C20	C15	9(2)	C16	C19	C20	C16	-0.0(14)
C16	C19	C20	C17	62.5(18)	C16	C19	C20	C21	82(2)
C18	C19	C20	C15	-99.9(18)	C18	C19	C20	C16	-109.3(14)
C18	C19	C20	C17	-46.8(13)	C18	C19	C20	C21	-27.2(14)
C15	C20	C21	O2	20.9(16)	C15	C20	C21	O3	37.9(15)
C15	C20	C21	C16	-49.1(11)	C15	C20	C21	C17	-64(2)
C16	C20	C21	O2	70(2)	C16	C20	C21	O3	87(2)
C16	C20	C21	C16	-0.0(14)	C16	C20	C21	C17	-15(2)
C19	C20	C21	O2	1.2(17)	C19	C20	C21	O3	18.3(16)
C19	C20	C21	C16	-68.7(13)	C19	C20	C21	C17	-83(2)

Symmetry Operators:

(1) $-X+1,-Y+1,-Z+1$

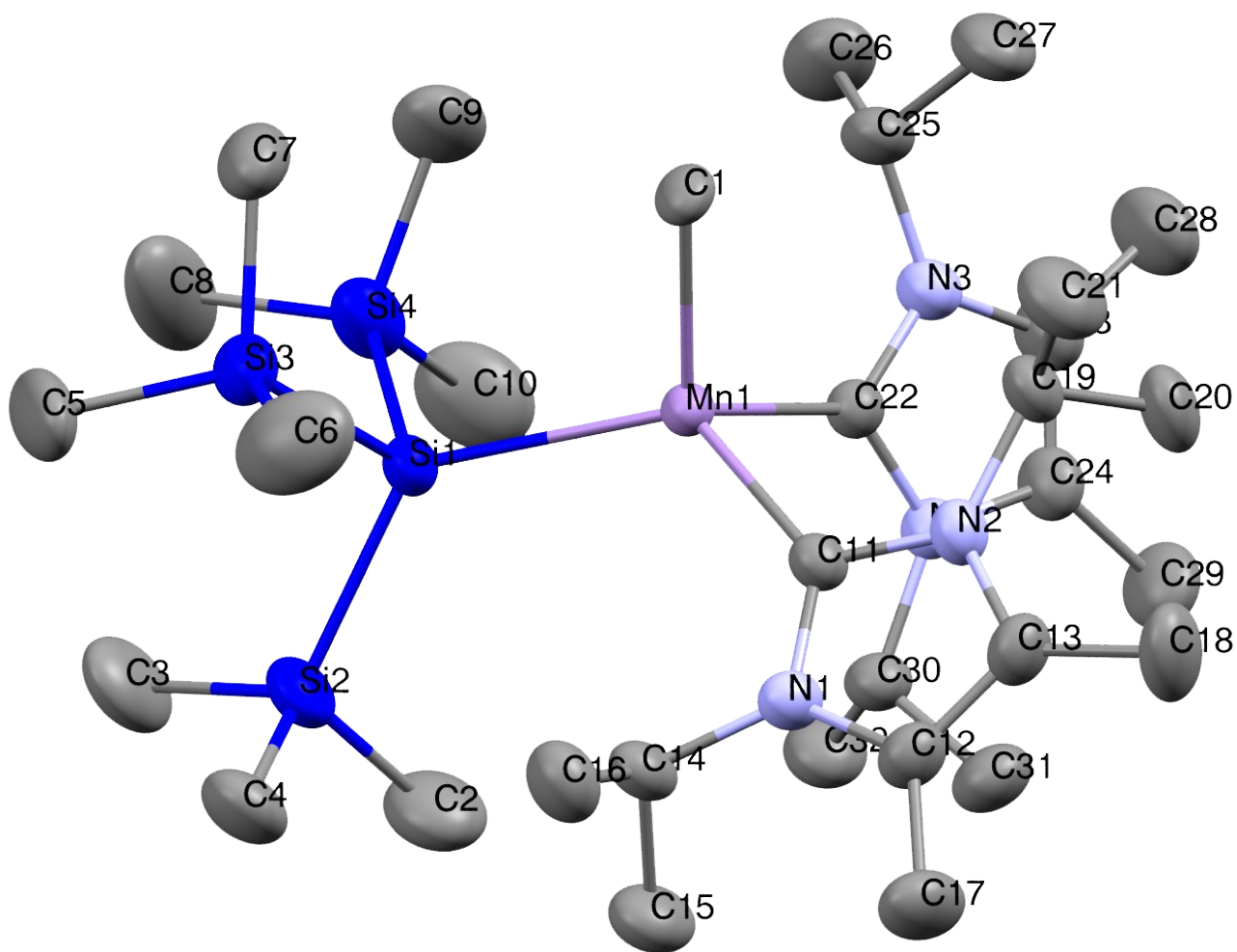


Figure S9. ORTEP drawing of **4** (50% probability of the thermal ellipsoids)

Table S3-1. Crystal data and structure refinement for **4**.

Empirical Formula	C ₃₂ H ₇₀ MnN ₄ Si ₄
Formula Weight	678.21
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.200 X 0.150 X 0.150 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 10.0789(16) Å b = 23.499(4) Å c = 18.131(3) Å β = 90.882(2) ° V = 4293.8(12) Å ³
Space Group	P2 ₁ /n (#14)
Z value	4
D _{calc}	1.049 g/cm ³
F ₀₀₀	1484.00
μ(MoKα)	4.423 cm ⁻¹
Diffractometer	Saturn724
Radiation	MoKα (λ = 0.71075 Å) multi-layer mirror monochromated
Voltage, Current	50kV, 24mA
Temperature	-69.8°C
Detector Aperture	72.8 x 72.8 mm
Data Images	720 exposures
ω oscillation Range (χ=45.0, φ=0.0)	-70.0 - 110.0°
Exposure Rate	4.0 sec./°
Detector Swing Angle	19.95°
ω oscillation Range (χ=45.0, φ=90.0)	-70.0 - 110.0°
Exposure Rate	4.0 sec./°
Detector Swing Angle	19.95°
Detector Position	44.81 mm
Pixel Size	0.141 mm
2θ _{max}	55.0°
No. of Reflections Measured	Total: 35096 Unique: 9686 (R _{int} = 0.1078)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.768 - 0.936)

Structure Solution	Direct Methods (SHELXT Version 2014/5)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1 / [\sigma^2(F_o^2) + (0.0671 \cdot P)^2 + 2.9677 \cdot P]$
	where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$
$2\theta_{\text{max}}$ cutoff	55.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	9686
No. Variables	370
Reflection/Parameter Ratio	26.18
Residuals: R1 ($I > 2.00\sigma(I)$)	0.0635
Residuals: R (All reflections)	0.0792
Residuals: wR2 (All reflections)	0.1754
Goodness of Fit Indicator	1.089
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.44 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.44 e ⁻ /Å ³

Table S3-2. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Mn1	0.67630(4)	0.32132(2)	0.28199(2)	2.246(10)
Si1	0.54155(8)	0.41303(3)	0.24015(4)	2.634(15)
Si2	0.48000(9)	0.49230(4)	0.30983(5)	3.732(18)
Si3	0.64308(10)	0.45369(4)	0.13731(5)	3.850(19)
Si4	0.33812(9)	0.37977(4)	0.19400(6)	4.22(2)
N1	0.9055(2)	0.36762(10)	0.40227(13)	2.73(4)
N2	0.9243(2)	0.27827(10)	0.38062(13)	2.73(4)
N3	0.5164(2)	0.20508(10)	0.32633(13)	2.94(4)
N4	0.5430(2)	0.25739(10)	0.42250(12)	2.65(4)
C1	0.7557(3)	0.28244(13)	0.18136(14)	2.82(5)
C2	0.4319(5)	0.4702(2)	0.4057(2)	6.18(10)
C3	0.3352(4)	0.53590(19)	0.2741(3)	6.61(11)
C4	0.6187(4)	0.54549(16)	0.3215(2)	5.14(8)
C5	0.5689(6)	0.52338(18)	0.1055(3)	7.22(13)
C6	0.8233(5)	0.4670(3)	0.1581(3)	7.41(13)
C7	0.6378(4)	0.40620(17)	0.05418(19)	5.09(8)
C8	0.2328(5)	0.4303(2)	0.1386(4)	8.58(16)
C9	0.3650(4)	0.31715(18)	0.1311(3)	5.67(9)
C10	0.2343(5)	0.3537(2)	0.2720(3)	7.33(13)
C11	0.8522(3)	0.32490(11)	0.36054(15)	2.43(4)
C12	1.0083(3)	0.34767(14)	0.44763(16)	3.10(5)
C13	1.0198(3)	0.29135(14)	0.43416(16)	3.14(5)
C14	0.8611(3)	0.42699(12)	0.39324(17)	3.08(5)
C15	0.8086(4)	0.45172(17)	0.4643(2)	4.65(7)
C16	0.9688(4)	0.46341(15)	0.3593(2)	4.38(7)
C17	1.0877(4)	0.38260(17)	0.5018(2)	4.55(7)
C18	1.1152(4)	0.25009(16)	0.4679(2)	4.89(8)
C19	0.8990(3)	0.22198(12)	0.34673(17)	3.15(5)
C20	0.8517(4)	0.17824(14)	0.4024(2)	4.23(7)
C21	1.0168(4)	0.20204(18)	0.3019(2)	5.09(8)
C22	0.5582(3)	0.25774(11)	0.34790(14)	2.45(4)
C23	0.4755(3)	0.17248(14)	0.38595(19)	3.62(6)
C24	0.4931(3)	0.20521(14)	0.44644(17)	3.36(5)
C25	0.5129(3)	0.18874(14)	0.24765(17)	3.57(6)
C26	0.3724(4)	0.17728(19)	0.2206(2)	5.63(9)
C27	0.6080(5)	0.13953(17)	0.2327(2)	5.29(8)
C28	0.4272(5)	0.11250(17)	0.3820(3)	5.79(9)

C29	0.4699(4)	0.18934(17)	0.5251(2)	4.75(8)
C30	0.5662(3)	0.30918(13)	0.46692(16)	2.98(5)
C31	0.6722(3)	0.30097(17)	0.52661(17)	4.03(6)
C32	0.4363(4)	0.33145(16)	0.4976(2)	4.41(7)

$$B_{\text{eq}} = 8/3 \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos \gamma + 2U_{13}(aa^*cc^*)\cos \beta + 2U_{23}(bb^*cc^*)\cos \alpha)$$

Table S3-3. Anisotropic displacement parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Mn1	0.0341(2)	0.0266(2)	0.0247(2)	0.00178(15)	0.00003(15)	0.00000(14)
Si1	0.0380(4)	0.0270(4)	0.0350(4)	0.0032(3)	-0.0027(3)	0.0009(3)
Si2	0.0522(5)	0.0328(4)	0.0568(6)	0.0115(4)	0.0022(4)	-0.0061(4)
Si3	0.0684(6)	0.0389(5)	0.0389(5)	-0.0057(4)	0.0004(4)	0.0078(4)
Si4	0.0433(5)	0.0417(5)	0.0747(7)	-0.0007(4)	-0.0166(5)	-0.0026(5)
N1	0.0314(12)	0.0370(13)	0.0352(12)	0.0015(10)	-0.0037(9)	-0.0042(10)
N2	0.0325(12)	0.0320(12)	0.0393(13)	0.0034(9)	-0.0015(10)	0.0026(10)
N3	0.0439(14)	0.0330(13)	0.0348(13)	-0.0041(10)	0.0049(10)	-0.0015(10)
N4	0.0360(12)	0.0354(13)	0.0294(12)	0.0002(10)	0.0054(9)	0.0014(9)
C1	0.0448(16)	0.0392(15)	0.0234(13)	0.0033(12)	0.0065(11)	0.0039(11)
C2	0.094(3)	0.074(3)	0.068(3)	0.007(2)	0.026(2)	-0.019(2)
C3	0.078(3)	0.057(3)	0.115(4)	0.035(2)	-0.013(3)	-0.017(3)
C4	0.081(3)	0.0392(19)	0.075(3)	-0.0036(18)	-0.002(2)	-0.0137(18)
C5	0.169(5)	0.042(2)	0.063(3)	0.008(3)	0.009(3)	0.018(2)
C6	0.082(3)	0.123(5)	0.077(3)	-0.041(3)	0.015(2)	0.006(3)
C7	0.095(3)	0.060(2)	0.0389(19)	0.016(2)	0.0020(18)	0.0042(16)
C8	0.090(3)	0.074(3)	0.160(5)	0.016(3)	-0.074(4)	-0.005(3)
C9	0.075(3)	0.063(3)	0.077(3)	-0.012(2)	-0.026(2)	-0.014(2)
C10	0.059(3)	0.092(4)	0.128(5)	-0.020(3)	0.021(3)	-0.015(3)
C11	0.0313(14)	0.0279(13)	0.0331(14)	0.0012(10)	0.0023(10)	-0.0022(10)
C12	0.0341(15)	0.0476(17)	0.0361(15)	-0.0011(13)	-0.0059(11)	0.0006(13)
C13	0.0341(15)	0.0457(17)	0.0393(16)	0.0004(13)	-0.0065(12)	0.0063(13)
C14	0.0392(16)	0.0322(14)	0.0455(17)	0.0043(12)	-0.0027(12)	-0.0097(12)
C15	0.065(2)	0.054(2)	0.058(2)	0.0125(18)	0.0033(17)	-0.0175(17)
C16	0.059(2)	0.0407(18)	0.067(2)	-0.0015(15)	-0.0005(17)	0.0018(16)
C17	0.051(2)	0.066(2)	0.055(2)	0.0044(17)	-0.0184(16)	-0.0140(18)
C18	0.052(2)	0.052(2)	0.081(3)	0.0041(16)	-0.0224(18)	0.0198(19)
C19	0.0433(16)	0.0285(14)	0.0479(17)	0.0047(12)	-0.0030(13)	-0.0009(12)
C20	0.057(2)	0.0315(16)	0.072(2)	0.0023(14)	-0.0061(17)	0.0106(15)
C21	0.062(2)	0.056(2)	0.075(3)	0.0106(18)	0.0112(19)	-0.012(2)
C22	0.0320(14)	0.0308(13)	0.0304(13)	0.0001(11)	0.0012(10)	0.0006(10)

C23	0.0523(19)	0.0364(16)	0.0490(19)	-0.0086(14)	0.0108(14)	0.0048(13)
C24	0.0465(18)	0.0396(16)	0.0418(17)	-0.0033(13)	0.0110(13)	0.0070(13)
C25	0.058(2)	0.0386(16)	0.0386(16)	-0.0063(14)	-0.0045(14)	-0.0080(13)
C26	0.078(3)	0.069(3)	0.066(3)	-0.027(2)	-0.016(2)	-0.001(2)
C27	0.100(3)	0.049(2)	0.052(2)	0.009(2)	0.008(2)	-0.0136(17)
C28	0.103(3)	0.045(2)	0.073(3)	-0.022(2)	0.019(2)	0.0045(19)
C29	0.073(3)	0.062(2)	0.046(2)	-0.0040(19)	0.0162(18)	0.0140(17)
C30	0.0429(16)	0.0392(16)	0.0313(14)	0.0003(12)	0.0018(12)	-0.0043(12)
C31	0.055(2)	0.063(2)	0.0348(16)	-0.0036(17)	-0.0052(14)	-0.0014(15)
C32	0.061(2)	0.058(2)	0.049(2)	0.0106(17)	0.0107(16)	-0.0090(16)

The general temperature factor expression: $\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl))$

Table S3-4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Mn1	Si1	2.6520(9)	Mn1	C1	2.202(3)
Mn1	C11	2.258(3)	Mn1	C22	2.263(3)
Si1	Si2	2.3399(12)	Si1	Si3	2.3443(12)
Si1	Si4	2.3371(13)	Si2	C2	1.884(5)
Si2	C3	1.889(5)	Si2	C4	1.885(4)
Si3	C5	1.887(5)	Si3	C6	1.876(5)
Si3	C7	1.876(4)	Si4	C8	1.874(6)
Si4	C9	1.883(4)	Si4	C10	1.876(5)
N1	C11	1.362(4)	N1	C12	1.394(4)
N1	C14	1.473(4)	N2	C11	1.361(3)
N2	C13	1.391(4)	N2	C19	1.479(4)
N3	C22	1.363(3)	N3	C23	1.392(4)
N3	C25	1.477(4)	N4	C22	1.364(3)
N4	C24	1.397(4)	N4	C30	1.476(4)
C12	C13	1.351(5)	C12	C17	1.502(5)
C13	C18	1.490(5)	C14	C15	1.515(5)
C14	C16	1.520(5)	C19	C20	1.523(5)
C19	C21	1.523(5)	C23	C24	1.349(5)
C23	C28	1.492(5)	C24	C29	1.496(5)
C25	C26	1.516(5)	C25	C27	1.529(5)
C30	C31	1.522(4)	C30	C32	1.523(5)

Table S3-5. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
Si1	Mn1	C1	106.93(8)	Si1	Mn1	C11	122.93(7)
Si1	Mn1	C22	114.61(7)	C1	Mn1	C11	104.26(10)
C1	Mn1	C22	111.37(10)	C11	Mn1	C22	96.06(10)
Mn1	Si1	Si2	129.15(4)	Mn1	Si1	Si3	109.32(4)
Mn1	Si1	Si4	105.86(4)	Si2	Si1	Si3	103.15(4)
Si2	Si1	Si4	102.77(5)	Si3	Si1	Si4	104.05(5)
Si1	Si2	C2	110.67(16)	Si1	Si2	C3	117.14(16)
Si1	Si2	C4	112.71(13)	C2	Si2	C3	104.9(2)
C2	Si2	C4	106.3(2)	C3	Si2	C4	104.26(19)
Si1	Si3	C5	114.93(17)	Si1	Si3	C6	109.96(17)
Si1	Si3	C7	112.92(13)	C5	Si3	C6	107.1(3)
C5	Si3	C7	105.32(19)	C6	Si3	C7	106.0(2)
Si1	Si4	C8	117.82(17)	Si1	Si4	C9	110.14(14)
Si1	Si4	C10	109.63(16)	C8	Si4	C9	104.8(2)
C8	Si4	C10	107.1(2)	C9	Si4	C10	106.7(2)
C11	N1	C12	111.3(2)	C11	N1	C14	121.3(2)
C12	N1	C14	127.3(2)	C11	N2	C13	111.7(2)
C11	N2	C19	121.4(2)	C13	N2	C19	126.9(2)
C22	N3	C23	111.8(2)	C22	N3	C25	121.0(2)
C23	N3	C25	127.1(3)	C22	N4	C24	111.1(2)
C22	N4	C30	121.1(2)	C24	N4	C30	127.5(2)
Mn1	C11	N1	132.58(19)	Mn1	C11	N2	123.32(18)
N1	C11	N2	103.9(2)	N1	C12	C13	106.8(3)
N1	C12	C17	125.9(3)	C13	C12	C17	127.4(3)
N2	C13	C12	106.4(3)	N2	C13	C18	125.3(3)
C12	C13	C18	128.3(3)	N1	C14	C15	112.2(3)
N1	C14	C16	111.2(2)	C15	C14	C16	112.9(3)
N2	C19	C20	112.5(3)	N2	C19	C21	111.5(3)
C20	C19	C21	113.6(3)	Mn1	C22	N3	127.66(19)
Mn1	C22	N4	126.60(18)	N3	C22	N4	103.9(2)
N3	C23	C24	106.3(3)	N3	C23	C28	125.7(3)
C24	C23	C28	128.0(3)	N4	C24	C23	106.9(3)
N4	C24	C29	125.3(3)	C23	C24	C29	127.8(3)
N3	C25	C26	111.5(3)	N3	C25	C27	111.3(3)
C26	C25	C27	113.1(3)	N4	C30	C31	112.8(3)
N4	C30	C32	110.7(2)	C31	C30	C32	112.4(3)

Table S3-6. Torsion Angles(^o)

(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
C1	Mn1	Si1	Si2	-159.88(9)	C1	Mn1	Si1	Si3	-33.26(9)
C1	Mn1	Si1	Si4	78.27(9)	Si1	Mn1	C11	N1	8.0(3)
Si1	Mn1	C11	N2	-178.01(14)	C11	Mn1	Si1	Si2	-39.62(10)
C11	Mn1	Si1	Si3	87.00(9)	C11	Mn1	Si1	Si4	-161.47(8)
Si1	Mn1	C22	N3	110.02(18)	Si1	Mn1	C22	N4	-88.05(19)
C22	Mn1	Si1	Si2	76.18(8)	C22	Mn1	Si1	Si3	-157.21(7)
C22	Mn1	Si1	Si4	-45.67(8)	C1	Mn1	C11	N1	129.5(2)
C1	Mn1	C11	N2	-56.5(2)	C1	Mn1	C22	N3	-11.5(2)
C1	Mn1	C22	N4	150.41(18)	C11	Mn1	C22	N3	-119.4(2)
C11	Mn1	C22	N4	42.5(2)	C22	Mn1	C11	N1	-116.6(2)
C22	Mn1	C11	N2	57.4(2)	Mn1	Si1	Si2	C2	-37.91(7)
Mn1	Si1	Si2	C3	-158.08(4)	Mn1	Si1	Si2	C4	80.96(6)
Mn1	Si1	Si3	C5	-174.66(4)	Mn1	Si1	Si3	C6	-53.74(5)
Mn1	Si1	Si3	C7	64.48(6)	Mn1	Si1	Si4	C8	-165.54(5)
Mn1	Si1	Si4	C9	-45.43(6)	Mn1	Si1	Si4	C10	71.73(5)
Si2	Si1	Si3	C5	-34.40(6)	Si2	Si1	Si3	C6	86.53(5)
Si2	Si1	Si3	C7	-155.25(5)	Si3	Si1	Si2	C2	-166.85(4)
Si3	Si1	Si2	C3	72.99(6)	Si3	Si1	Si2	C4	-47.97(6)
Si2	Si1	Si4	C8	56.94(7)	Si2	Si1	Si4	C9	177.06(5)
Si2	Si1	Si4	C10	-65.78(5)	Si4	Si1	Si2	C2	85.17(5)
Si4	Si1	Si2	C3	-34.99(6)	Si4	Si1	Si2	C4	-155.96(5)
Si3	Si1	Si4	C8	-50.35(7)	Si3	Si1	Si4	C9	69.76(6)
Si3	Si1	Si4	C10	-173.08(4)	Si4	Si1	Si3	C5	72.62(6)
Si4	Si1	Si3	C6	-166.46(4)	Si4	Si1	Si3	C7	-48.24(6)
C11	N1	C12	C13	0.0(3)	C11	N1	C12	C17	-178.8(2)
C12	N1	C11	Mn1	174.5(2)	C12	N1	C11	N2	-0.3(3)
C11	N1	C14	C15	121.9(2)	C11	N1	C14	C16	-110.6(3)
C14	N1	C11	Mn1	-9.6(4)	C14	N1	C11	N2	175.5(2)
C12	N1	C14	C15	-62.9(3)	C12	N1	C14	C16	64.6(3)
C14	N1	C12	C13	-175.5(2)	C14	N1	C12	C17	5.6(4)
C11	N2	C13	C12	-0.5(3)	C11	N2	C13	C18	-179.9(2)
C13	N2	C11	Mn1	-174.95(19)	C13	N2	C11	N1	0.5(3)
C11	N2	C19	C20	-116.4(3)	C11	N2	C19	C21	114.7(3)
C19	N2	C11	Mn1	5.5(3)	C19	N2	C11	N1	-179.1(2)
C13	N2	C19	C20	64.1(3)	C13	N2	C19	C21	-64.8(3)
C19	N2	C13	C12	179.0(2)	C19	N2	C13	C18	-0.4(4)

C22	N3	C23	C24	-0.5(3)	C22	N3	C23	C28	-178.4(2)
C23	N3	C22	Mn1	165.3(2)	C23	N3	C22	N4	0.1(3)
C22	N3	C25	C26	-115.9(3)	C22	N3	C25	C27	116.7(3)
C25	N3	C22	Mn1	-16.9(4)	C25	N3	C22	N4	177.9(2)
C23	N3	C25	C26	61.5(4)	C23	N3	C25	C27	-65.9(4)
C25	N3	C23	C24	-178.1(2)	C25	N3	C23	C28	4.0(5)
C22	N4	C24	C23	-0.6(3)	C22	N4	C24	C29	177.2(2)
C24	N4	C22	Mn1	-165.0(2)	C24	N4	C22	N3	0.3(3)
C22	N4	C30	C31	-121.9(2)	C22	N4	C30	C32	111.2(3)
C30	N4	C22	Mn1	20.3(3)	C30	N4	C22	N3	-174.3(2)
C24	N4	C30	C31	64.4(3)	C24	N4	C30	C32	-62.5(3)
C30	N4	C24	C23	173.6(2)	C30	N4	C24	C29	-8.5(4)
N1	C12	C13	N2	0.3(3)	N1	C12	C13	C18	179.7(2)
C17	C12	C13	N2	179.1(3)	C17	C12	C13	C18	-1.5(5)
N3	C23	C24	N4	0.7(3)	N3	C23	C24	C29	-177.1(3)
C28	C23	C24	N4	178.5(3)	C28	C23	C24	C29	0.7(6)

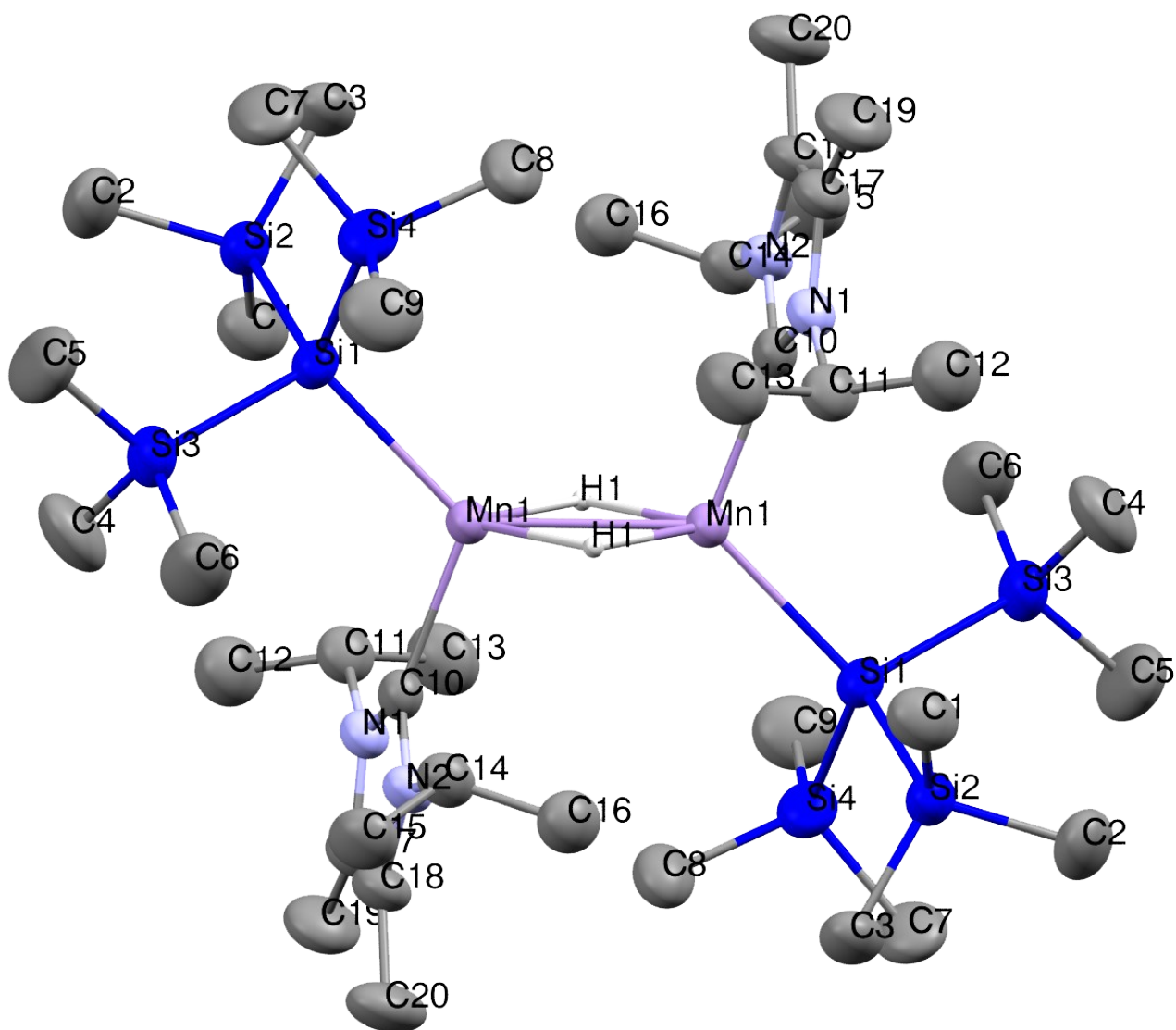


Figure S10. ORTEP drawing of **5** (50% probability of the thermal ellipsoids)

Table S4-1. Crystal data and structure refinement for **5**.

Empirical Formula	C ₄₀ H ₉₆ Mn ₂ N ₄ Si ₈
Formula Weight	967.79
Crystal Color, Habit	orange, platelet
Crystal Dimensions	0.100 X 0.050 X 0.050 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 9.769(4) Å b = 12.962(5) Å c = 14.713(5) Å $\alpha = 97.083(5)^\circ$ $\beta = 97.254(5)^\circ$ $\gamma = 108.321(5)^\circ$ V = 1727.9(11) Å ³
Space Group	P-1 (#2)
Z value	2
D _{calc}	1.860 g/cm ³
F ₀₀₀	1052.00
μ (MoK α)	10.549 cm ⁻¹
Diffractometer	Saturn724
Radiation	MoK α ($\lambda = 0.71075$ Å) multi-layer mirror monochromated
Voltage, Current	50kV, 24mA
Temperature	-69.8°C
Detector Aperture	72.8 x 72.8 mm
Data Images	720 exposures
ω oscillation Range ($\chi=45.0$, $\phi=0.0$)	-70.0 - 110.0°
Exposure Rate	120.0 sec./°
Detector Swing Angle	19.96°
ω oscillation Range ($\chi=45.0$, $\phi=90.0$)	-70.0 - 110.0°
Exposure Rate	120.0 sec./°
Detector Swing Angle	19.96°
Detector Position	44.77 mm
Pixel Size	0.141 mm
2 θ _{max}	55.1°
No. of Reflections Measured	Total: 14394 Unique: 7646 (R _{int} = 0.1324)
Corrections	Lorentz-polarization Absorption

Structure Solution	(trans. factors: 0.761 - 0.949) Direct Methods (SHELXT Version 2014/5)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1 / [\sigma^2(F_o^2) + (0.1098 \cdot P)^2 + 0.0000 \cdot P]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$
$2\theta_{\text{max}}$ cutoff	55.1°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	7644
No. Variables	248
Reflection/Parameter Ratio	30.82
Residuals: R1 ($I > 2.00\sigma(I)$)	0.0714
Residuals: R (All reflections)	0.1030
Residuals: wR2 (All reflections)	0.2151
Goodness of Fit Indicator	1.029
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.78 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.62 e ⁻ /Å ³

Table S4-2. Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$

atom	x	y	z	B_{eq}
Mn1	0.56572(6)	0.50665(4)	0.59166(4)	2.442(13)
Si1	0.53689(12)	0.37010(8)	0.70793(7)	2.74(2)
Si2	0.36436(13)	0.35125(9)	0.80780(8)	3.26(2)
Si3	0.76209(14)	0.42277(10)	0.80825(8)	3.88(2)
Si4	0.50286(15)	0.19105(9)	0.63576(9)	3.73(2)
N1	0.7101(4)	0.7556(2)	0.6950(2)	2.89(5)
N2	0.8589(3)	0.7155(2)	0.6131(2)	3.04(5)
C1	0.3285(6)	0.4848(4)	0.8349(4)	4.78(10)
C2	0.4251(6)	0.3140(5)	0.9213(4)	5.48(11)
C3	0.1830(5)	0.2412(4)	0.7610(4)	4.74(9)
C4	0.7871(7)	0.5478(5)	0.8964(4)	6.75(14)
C5	0.7989(8)	0.3169(6)	0.8753(5)	8.05(18)
C6	0.9138(6)	0.4620(5)	0.7398(4)	6.28(13)
C7	0.4683(7)	0.0854(4)	0.7152(4)	5.70(12)
C8	0.3417(6)	0.1415(4)	0.5377(4)	4.91(10)
C9	0.6679(6)	0.1852(4)	0.5834(4)	5.98(13)
C10	0.7314(4)	0.6702(3)	0.6419(2)	2.73(6)
C11	0.5802(5)	0.7376(3)	0.7393(3)	3.58(7)
C12	0.6187(6)	0.7865(4)	0.8422(4)	5.46(11)
C13	0.4677(6)	0.7753(4)	0.6867(4)	5.29(11)
C14	0.9188(5)	0.6467(3)	0.5525(3)	3.44(7)
C15	1.0772(5)	0.6602(4)	0.5901(4)	4.77(9)
C16	0.8973(6)	0.6660(4)	0.4531(3)	4.61(9)
C17	0.8219(5)	0.8534(3)	0.6958(3)	3.62(7)
C18	0.9159(5)	0.8291(3)	0.6445(3)	3.79(8)
C19	0.8284(6)	0.9642(3)	0.7433(4)	5.47(11)
C20	1.0525(6)	0.9046(4)	0.6221(4)	5.78(12)

$$B_{\text{eq}} = 8/3 \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos \gamma + 2U_{13}(aa^*cc^*)\cos \beta + 2U_{23}(bb^*cc^*)\cos \alpha)$$

Table S4-3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn1	0.0311(3)	0.0298(3)	0.0303(3)	0.0090(2)	0.0029(2)	0.0050(2)
Si1	0.0384(6)	0.0352(5)	0.0336(5)	0.0151(4)	0.0067(4)	0.0094(4)
Si2	0.0428(7)	0.0470(6)	0.0340(6)	0.0133(5)	0.0096(5)	0.0089(4)
Si3	0.0413(7)	0.0635(7)	0.0439(6)	0.0195(6)	0.0011(5)	0.0159(5)
Si4	0.0585(8)	0.0363(6)	0.0531(7)	0.0226(5)	0.0124(6)	0.0097(5)
N1	0.0370(17)	0.0322(15)	0.0369(16)	0.0101(13)	0.0018(14)	0.0013(12)

N2	0.0321(17)	0.0381(16)	0.0399(17)	0.0057(13)	0.0049(14)	0.0039(13)
C1	0.058(3)	0.058(3)	0.064(3)	0.020(2)	0.021(3)	-0.002(2)
C2	0.067(4)	0.095(4)	0.049(3)	0.023(3)	0.018(3)	0.025(3)
C3	0.046(3)	0.065(3)	0.060(3)	0.002(2)	0.014(2)	0.015(2)
C4	0.067(4)	0.091(4)	0.069(4)	0.007(3)	-0.012(3)	-0.020(3)
C5	0.079(5)	0.122(5)	0.111(5)	0.030(4)	-0.005(4)	0.071(4)
C6	0.044(3)	0.111(4)	0.093(4)	0.029(3)	0.015(3)	0.040(4)
C7	0.084(4)	0.041(2)	0.096(4)	0.026(3)	0.006(3)	0.025(2)
C8	0.077(4)	0.046(2)	0.057(3)	0.019(2)	0.001(3)	-0.001(2)
C9	0.078(4)	0.065(3)	0.095(4)	0.038(3)	0.031(3)	-0.001(3)
C10	0.0331(19)	0.0392(18)	0.0319(18)	0.0136(15)	0.0036(15)	0.0067(14)
C11	0.049(2)	0.043(2)	0.045(2)	0.0185(19)	0.0102(19)	-0.0005(17)
C12	0.070(4)	0.076(3)	0.060(3)	0.023(3)	0.019(3)	0.003(3)
C13	0.051(3)	0.072(3)	0.083(4)	0.032(3)	0.007(3)	0.004(3)
C14	0.034(2)	0.049(2)	0.047(2)	0.0138(17)	0.0117(18)	0.0032(18)
C15	0.036(2)	0.071(3)	0.076(3)	0.018(2)	0.013(2)	0.020(3)
C16	0.059(3)	0.064(3)	0.052(3)	0.018(2)	0.018(2)	0.007(2)
C17	0.044(2)	0.0349(19)	0.049(2)	0.0042(17)	0.0023(19)	-0.0003(17)
C18	0.038(2)	0.039(2)	0.055(3)	0.0002(17)	0.0019(19)	0.0050(18)
C19	0.076(4)	0.038(2)	0.080(4)	0.008(2)	0.010(3)	-0.008(2)
C20	0.062(3)	0.051(3)	0.084(4)	-0.010(2)	0.021(3)	-0.002(2)

The general temperature factor expression: $\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl))$

Table S4-4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Mn1	Mn1 ¹	2.7972(12)	Mn1	Si1	2.5871(14)
Mn1	C10	2.194(3)	Si1	Si2	2.3482(19)
Si1	Si3	2.3391(17)	Si1	Si4	2.3329(18)
Si2	C1	1.877(5)	Si2	C2	1.872(6)
Si2	C3	1.873(4)	Si3	C4	1.877(6)
Si3	C5	1.882(8)	Si3	C6	1.870(6)
Si4	C7	1.887(6)	Si4	C8	1.880(5)
Si4	C9	1.891(7)	N1	C10	1.361(5)
N1	C11	1.466(6)	N1	C17	1.387(4)
N2	C10	1.345(5)	N2	C14	1.482(6)
N2	C18	1.394(5)	C11	C12	1.518(7)
C11	C13	1.503(8)	C14	C15	1.523(7)
C14	C16	1.515(7)	C17	C18	1.345(7)
C17	C19	1.496(6)	C18	C20	1.489(7)

Mn1 H1 1.91(3) Mn1 H1¹ 1.99(3)

Symmetry Operators:

(1) -X+1,-Y+1,-Z+1

Table S4-5. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
Mn1 ¹	Mn1	Si1	134.23(3)	Mn1 ¹	Mn1	C10	110.02(10)
Si1	Mn1	C10	115.74(10)	Mn1	Si1	Si2	122.34(6)
Mn1	Si1	Si3	106.68(5)	Mn1	Si1	Si4	112.26(6)
Si2	Si1	Si3	104.21(6)	Si2	Si1	Si4	105.50(6)
Si3	Si1	Si4	104.19(7)	Si1	Si2	C1	109.78(18)
Si1	Si2	C2	113.4(2)	Si1	Si2	C3	114.86(18)
C1	Si2	C2	107.3(3)	C1	Si2	C3	107.2(2)
C2	Si2	C3	103.8(2)	Si1	Si3	C4	111.0(2)
Si1	Si3	C5	117.14(19)	Si1	Si3	C6	109.33(19)
C4	Si3	C5	106.5(3)	C4	Si3	C6	106.6(3)
C5	Si3	C6	105.6(3)	Si1	Si4	C7	114.42(18)
Si1	Si4	C8	110.87(18)	Si1	Si4	C9	111.00(16)
C7	Si4	C8	106.4(2)	C7	Si4	C9	107.0(3)
C8	Si4	C9	106.7(3)	C10	N1	C11	120.6(3)
C10	N1	C17	110.3(3)	C11	N1	C17	129.0(3)
C10	N2	C14	120.5(3)	C10	N2	C18	111.4(3)
C14	N2	C18	128.0(3)	Mn1	C10	N1	125.1(3)
Mn1	C10	N2	128.7(3)	N1	C10	N2	104.8(3)
N1	C11	C12	112.3(4)	N1	C11	C13	111.1(4)
C12	C11	C13	113.2(5)	N2	C14	C15	112.7(3)
N2	C14	C16	111.0(4)	C15	C14	C16	112.6(4)
N1	C17	C18	107.4(3)	N1	C17	C19	124.4(4)
C18	C17	C19	128.2(4)	N2	C18	C17	106.0(3)
N2	C18	C20	125.0(4)	C17	C18	C20	128.9(4)

Symmetry Operators:

(1) -X+1,-Y+1,-Z+1

Table S4-6. Torsion Angles(°)

(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
Mn1 ¹	Mn1	Si1	Si2	-88.30(6)	Mn1 ¹	Mn1	Si1	Si3	152.17(4)
Mn1 ¹	Mn1	Si1	Si4	38.64(8)	Si1	Mn1	Mn1 ¹	Si1 ¹	180.00(5)
Si1	Mn1	Mn1 ¹	C10 ¹	1.47(6)	Mn1 ¹	Mn1	C10	N1	97.9(3)

Mn1 ¹	Mn1	C10	N2	-66.6(3)	C10	Mn1	Mn1 ¹	Si1 ¹	-1.47(13)
C10	Mn1	Mn1 ¹	C10 ¹	180.00(12)	Si1	Mn1	C10	N1	-83.2(3)
Si1	Mn1	C10	N2	112.2(3)	C10	Mn1	Si1	Si2	93.23(13)
C10	Mn1	Si1	Si3	-26.31(14)	C10	Mn1	Si1	Si4	-139.84(13)
Mn1	Si1	Si2	C1	-28.54(7)	Mn1	Si1	Si2	C2	-148.49(5)
Mn1	Si1	Si2	C3	92.34(8)	Mn1	Si1	Si3	C4	76.60(8)
Mn1	Si1	Si3	C5	-160.81(6)	Mn1	Si1	Si3	C6	-40.77(8)
Mn1	Si1	Si4	C7	-176.06(6)	Mn1	Si1	Si4	C8	-55.77(8)
Mn1	Si1	Si4	C9	62.70(8)	Si2	Si1	Si3	C4	-54.08(8)
Si2	Si1	Si3	C5	68.50(9)	Si2	Si1	Si3	C6	-171.45(6)
Si3	Si1	Si2	C1	92.17(7)	Si3	Si1	Si2	C2	-27.77(8)
Si3	Si1	Si2	C3	-146.95(7)	Si2	Si1	Si4	C7	-40.55(9)
Si2	Si1	Si4	C8	79.73(8)	Si2	Si1	Si4	C9	-161.80(6)
Si4	Si1	Si2	C1	-158.40(6)	Si4	Si1	Si2	C2	81.66(7)
Si4	Si1	Si2	C3	-37.51(9)	Si3	Si1	Si4	C7	68.89(9)
Si3	Si1	Si4	C8	-170.82(6)	Si3	Si1	Si4	C9	-52.35(8)
Si4	Si1	Si3	C4	-164.47(6)	Si4	Si1	Si3	C5	-41.89(9)
Si4	Si1	Si3	C6	78.16(8)	C10	N1	C11	C12	129.7(3)
C10	N1	C11	C13	-102.3(4)	C11	N1	C10	Mn1	12.6(5)
C11	N1	C10	N2	-179.8(3)	C10	N1	C17	C18	-1.3(4)
C10	N1	C17	C19	176.6(3)	C17	N1	C10	Mn1	-165.5(3)
C17	N1	C10	N2	2.1(4)	C11	N1	C17	C18	-179.2(3)
C11	N1	C17	C19	-1.3(6)	C17	N1	C11	C12	-52.5(5)
C17	N1	C11	C13	75.4(4)	C10	N2	C14	C15	-128.1(3)
C10	N2	C14	C16	104.6(4)	C14	N2	C10	Mn1	-12.8(5)
C14	N2	C10	N1	-179.8(3)	C10	N2	C18	C17	1.4(4)
C10	N2	C18	C20	-177.6(3)	C18	N2	C10	Mn1	164.9(3)
C18	N2	C10	N1	-2.1(4)	C14	N2	C18	C17	178.9(3)
C14	N2	C18	C20	-0.1(6)	C18	N2	C14	C15	54.6(5)
C18	N2	C14	C16	-72.7(5)	N1	C17	C18	N2	-0.1(5)
N1	C17	C18	C20	178.9(4)	C19	C17	C18	N2	-177.9(4)
C19	C17	C18	C20	1.1(8)					

Symmetry Operators:

(1) -X+1,-Y+1,-Z+1

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