Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Hemicubane topological analogs of the oxygen-evolving complex of photosystem II mediating water-assisted propylene carbonate oxidation

Connor Koellner, Michael R. Gau, Aleksander Polyak, Manish Bayana, Michael J. Zdilla*

Contents

Experimental

General

All operations were carried out under an air-free nitrogen atmosphere inside of a glovebox. All solvents were distilled from sodium benzophenone ketyl under nitrogen atmosphere and stored over activated molecular sieves for 24 h prior to use. UV-vis spectra were collected on Shimadzu UV-1800 using THF as solvent. IR spectra were collected on Thermo Scientific Nicolet iS5 transmission iD1 pressed in a KBr pellet. CHN analysis was provided by the CENTC Elemental Analysis Facility at University of Rochester. X-ray crystallographic data was collected on Bruker Apex Duo using Mo Kα radiation at 100K, cooled with an oxford cryostream 700. Structural models were refined using the SHELX package[44] with Olex2[45] as a GUI. Squeeze was implemented for solvent flattening using PLATON.[46] Electrochemistry was performed using CHI630 potentiostat.

Electrochemistry

Electrochemical experiments were performed using cyclic voltammetry with a standard three-electrode set-up with a silver/silver chloride wire as a pseudoreference electrode, a platinum wire counter electrode, and a glassy carbon working electrode. For comparison of electrochemical activities at equimolar molecular ratios, solutions were prepared in 3.5 mL of an electrolyte of 0.1 M tetrabutylammonium hexaflurophosphate in propylene carbonate. Hemicubane catalyst loadings were prepared as 1 mM solutions of $PyCH_2OH$ and compounds **1**-**5** in the electrolyte. Propylene carbonate decomposition experiments incorporated increasing concentrations of deionized water (0, 0.5, 1, and 3 %v/v). For comparison of electrochemical activities at equal ligand loadings, ligand loadings were also prepared as 6 mM, 10 mM, and 12 mM in distilled propylene carbonate with 0.1 M tetrabutylammonium hexafluorophosphate. Initial cyclic voltammograms were collected with 0% H_2O by volume, and additionally with 1% H_2O by volume. Solutions were sparged with N_2 gas overnight before the measurement of voltammograms. Due to air sensitivity of dilute solutions, voltammograms were generally measured at 1 V/s for electrocatalytic reactions due to current independence on scan rate at fast scan rates.

Synthesis

$Mn(NR_2)_2(THF)_2$ and $Ca(NR_2)_2(THF)_2$ were prepared using published procedures.[47,48]

*General procedure for synthesis of **1**-**5***

To a solution of bis(bis(trimethylsilyl)amido precursors (Mn or Mn/Ca) in 0.75 mL THF, a solution of 2-pyridinemethanol (116 μL, 1.2 mmol) in 0.25 mL THF was added dropwise. After mixing, the gold-colored solution was placed in a double-vial vapor diffusion apparatus with pentane as precipitating solvent, and was stored at -30°C, yielding gold crystalline product, which was isolated by decanting the mother liquor, and rinsing with cold pentane. This procedure was carried out using the following masses to obtain each product, described below.

*$Mn_4(PyCH_2O)_6(NR_2)_2 \cdot 0.5$ THF (**1**$\cdot 0.5$ THF)*, $Mn(NR_2)_2(THF)_2$ (180 mg, 0.346 mmol). Yield: 110 mg (0.090 mmol, >99%). FTIR (nm): 3053, 3012, 2811, 2775, 2686 (C-H stretch),1599, 1568, 1479, 1431, 1359, 1285, 1212, 1151, 1124 (C-H bend), 1085, 1046 (Si-N-Si asymm. Stretch),

1010, 993, 812 (C-H bend), 753, 725, 647, 634, 600, (C-O stretch), 488, 458 (Mn-O stretch). Unit cell (XRD): monoclinic P, *a* = 13.028(5) Å, *b* 11.850(4) Å, *c* = 20.643(7) Å, β = 93.358(7)°, *V* = 3181(2) Å^3.

*$CaMn_3(PyCH_2O)_6(NR_2)_2(THF)\cdot THF$ (**2**·THF)*, $Mn(NR_2)_2(THF)_2$ (180 mg, 0.346 mmol) and $Ca(NR_2)_2(THF)_2$ (35 mg, 0.069 mmol). Yield: 120 mg (0.090mmol, >99%). FTIR (nm): 3055, 3015, 2948, 2887, 2811, 2772, 2686 (C-H stretch), 1599, 1568, 1479, 1431, 1360, 1285, 1212, 1135, 1121 (C-H bend), 1088, 1046 (Si-N-Si asymm. Stretch), 1011, 932, 827, 823 (C-H bend), 753, 725, 634 (C-O stretch), 481, 459 (Mn-O stretch). Anal. Calcd for $C_{48}H_{72}CaMn_3N_8O_6Si_4\cdot 0.3\ C_4H_8O$ (%): C, 49.409; H, 6.270; N, 9.37. Found: C, 48.556; H, 6.373; N, 8.775. Unit cell (XRD): monoclinic P, *a* 10.5216(15) Å, *b* = 19.661(3) Å, *c* = 32.220(5) Å, β = 93.239(3)° , *V* = 6654.5(17) Å^3.

*$CaMn_5(PyCH_2O)_{10}\cdot 7\ THF$ (**3**·7 THF)*, $Mn(NR_2)_2(THF)_2$ (180 mg, 0.346 mmol) and $Ca(NR_2)_2(THF)_2\cdot 7$ THF (22 mg, 0.044 mmol). Yield: 110 mg (50 mmol, >99%). FTIR (nm): 3051, 3009, 2764, 2681 (C-H stretch), 1596, 1567, 1478, 1430, 1357, 1285, 1211, 1137, 1124 (C-H bend), 1086, 1045 (Si-N-Si asymm. Stretch), 995, 993, 753, 724, 632 (C-O stretch), 482, 453 (Mn-O stretch). Anal. Calcd for $C_{72}H_{96}CaMn_5N_{12}O_{10}Si_4$ (%): C, 50.373; H, 5.636; N, 9.791. Found: C, 50.161; H, 5.838; N, 9.412. Unit cell (XRD): monoclinic P, *a* = 15.598(4) Å, *b* = 16.828(4) Å, *c* = 43.150(11) Å, β = 91.079(5)° , *V* = 11,324(5) Å^3.

*$Ca_2Mn_4(PyCH_2O)_{10}(NR_2)_2\cdot 5\ THF$ (**4**·5 THF)*, $Mn(NR_2)_2(THF)_2$ (180 mg, 0.346 mmol) and $Ca(NR_2)_2(THF)_2$ (87 mg, 0.172 mmol). Yield: 110 mg (0.055 mmol, 64%); FTIR (nm): 3053, 3012, 2950, 2885, 2881, 2764, 2680 (C-H stretch), 1598, 1568, 1478, 1429, 1359, 1285, 1247, 1211, 1137, 1125 (C-H bend), 1087, 1045 (Si-N-Si asymm. Stretch), 1008, 930, 838, 821 (C-H bend), 752, 725, 638, 633 (C-O stretch), 482, 456 (Mn-O stretch). Unit cell (XRD): triclinic, *a* = 13.071(4) Å, *b* = 14.016(5) Å, *c* = 15.223(5) Å, α = 79.579(5)°, β = 73.067(5)° , γ = 83.215(5)°, *V* = 2617.6(15) Å^3.

*$[Ca_4Mn_3(PyCH_2O)_{12}(THF)_3][Mn(NR_2)_3]\cdot 7.5\ THF$ (**5**·7.5 THF)*, $Mn(NR_2)_2(THF)_2$ (180 mg, 0.346 mmol) and $Ca(NR_2)_2(THF)_2$ (173 mg, 0.342 mmol). Yield: 130 mg (0.040 mmol, 47%). FTIR (nm): 3053, 3009, 2975, 2765, 2680 (C-H stretch), 1596, 1568, 1477, 1429, 1360, 1285, 1211, 1135, 1124 (C-H bend), 1088, 1045 (Si-N-Si asymm. Stretch), 1001, 993, 821 (C-H bend), 751, 725, 639, 634 (C-O stretch), 476, 457 Mn-O stretch). Anal. Calcd for **5** – 1 THF (%): $C_{116}H_{196}Ca_4Mn_5N_{18}O_{14}Si_{12}$: C, 49.076; H, 6.959; N, 8.881. Found: C, 48.966; H, 7.315; N, 8.790. Unit cell (XRD): triclinic, *a* = 19.429(2) Å, *b* = 22.050(2) Å, *c* = 23.108(3) Å, 87.300(2)°, β = 66.466(2)° , γ = 71.707(2)°, *V* = 8582.7(16) Å^3.

EPR Spectroscopy

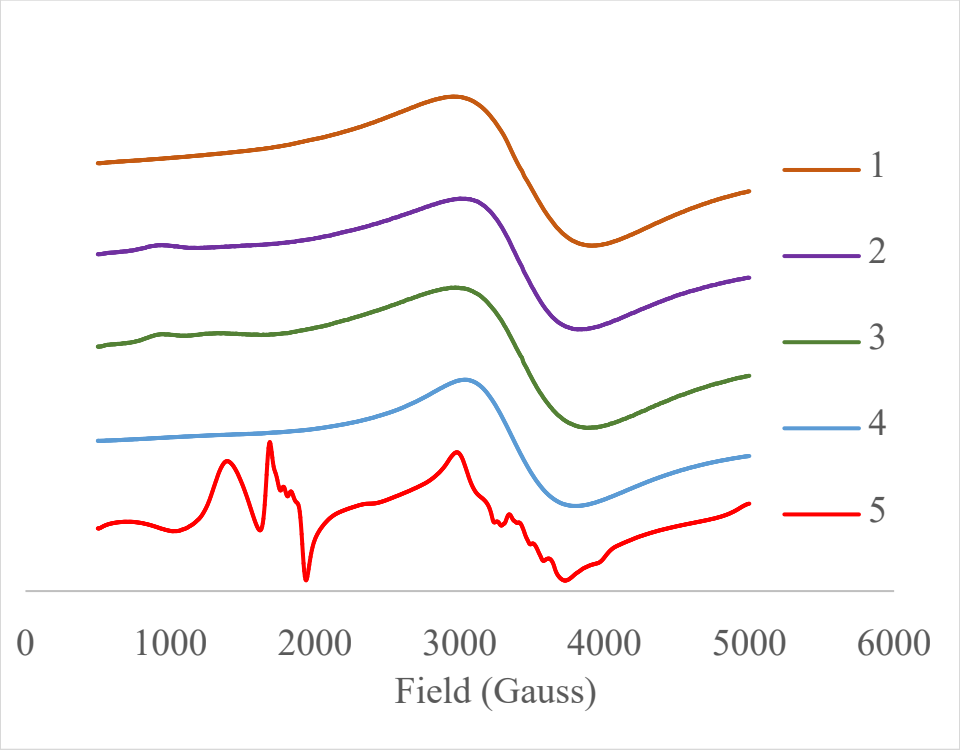


Figure S1. X-band EPR spectra of 1-5. MW Freq = 9.64 GHz Mod Amp = 4 G. MW Power: **1**-**3**, 2.01 mW; **4**, 6.36 mW; **5**, 0.201 mW.

UV-Visible absorption spectra.

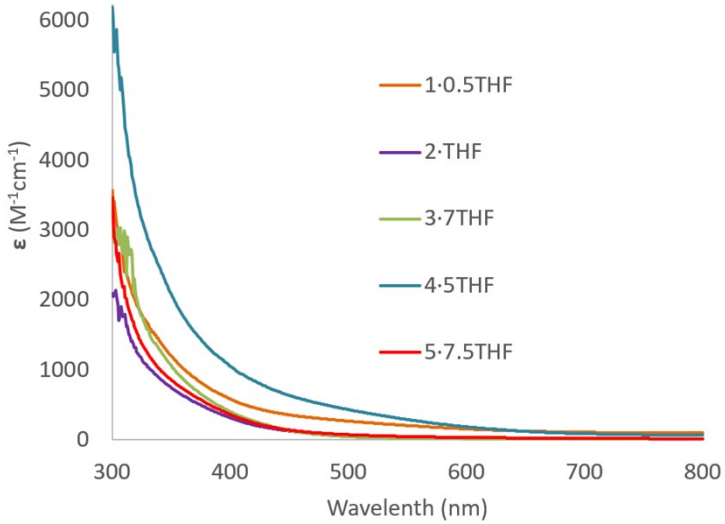


Figure S2. UV-Visible absorption spectra of compounds **1-5**.

Electrochemistry

Of interest for any OEC topological model is electrochemical water activation. However, compounds 1-5 are insoluble in water, and as such, cosolvents are required to test their reactivity. Inspired by the success of Agapie with oxidizing water to peroxide in propylene carbonate co-solvent,[13] we explored this approach for the above cluster systems. Propylene carbonate is a good solvent choice due to its electrochemical robustness, decomposing only above 1.5 V vs. NHE (Figure S3), which makes it of utility as an electrolyte in high-voltage lithium batteries.[57] In the absence of water, compounds 1-5 all exhibit fairly featureless cyclic voltammograms, suggesting manganese(II) in this ligand template is stable to reduction even to -2 V vs. NHE. (Figure S4).

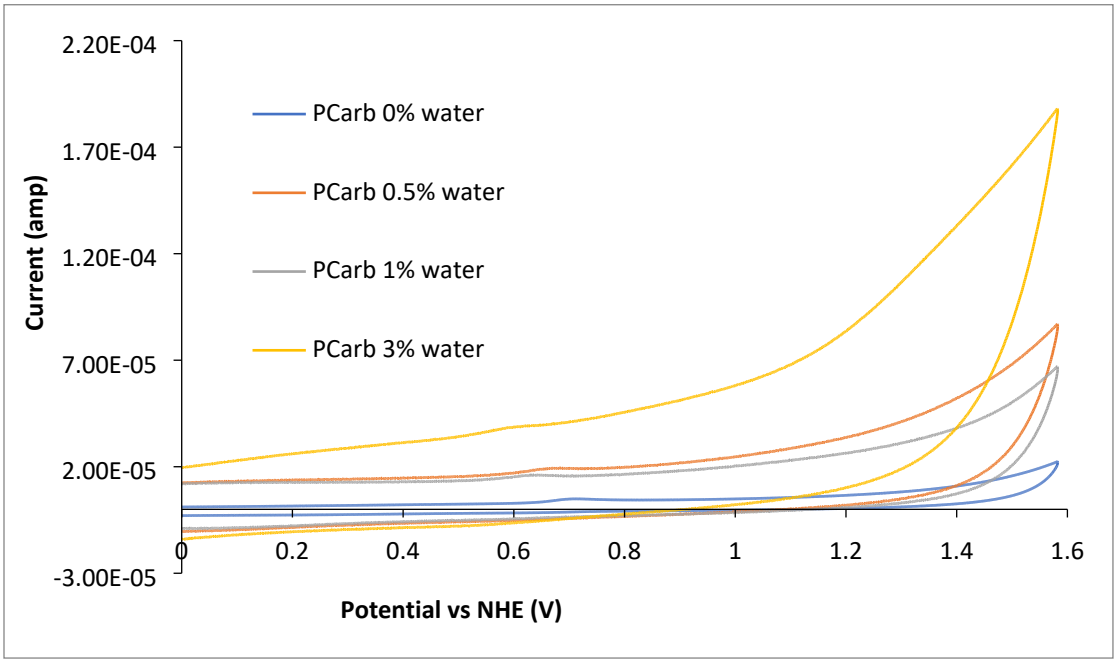


Figure S3. Cyclic voltammetry (0.3 V/s) of propylene carbonate in the absence, and presence of small percentages of water. A small impurity with a wave around 0.6 V is present in the solvent (even following distillation).

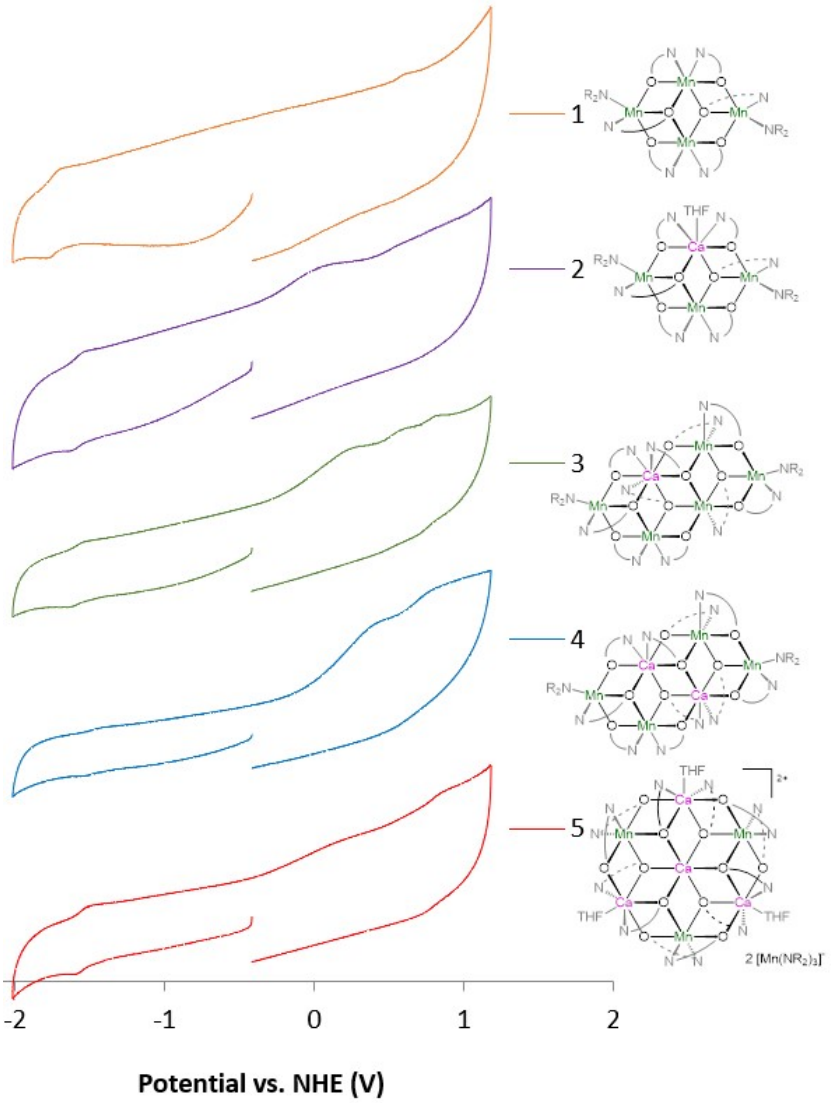


Figure S4. Cyclic voltammograms (0.5 V/s) of compounds **1**-**5** in dry propylene carbonate solvent.

We observed a catalytic current on the anodic side of the cyclic voltammetry for compounds **2-4** in the presence of 1% water (Figure S5) and a catalytic current (though less than that for **2-4**) became apparent for **1** and **5** as well at increasing water concentrations (Figure S6). No catalytic current is observed in the absence of catalyst (Figure S5), nor in the absence of water (Figures S7, S8), which rules out ligand decomposition as the cause of the anodic current. In the cases of all clusters, the electrocatalytic current increases with increasing concentrations of water at a controlled concentration of cluster, indicating electrocatalytic activation of water as being requisite in the generation of the catalytic current.

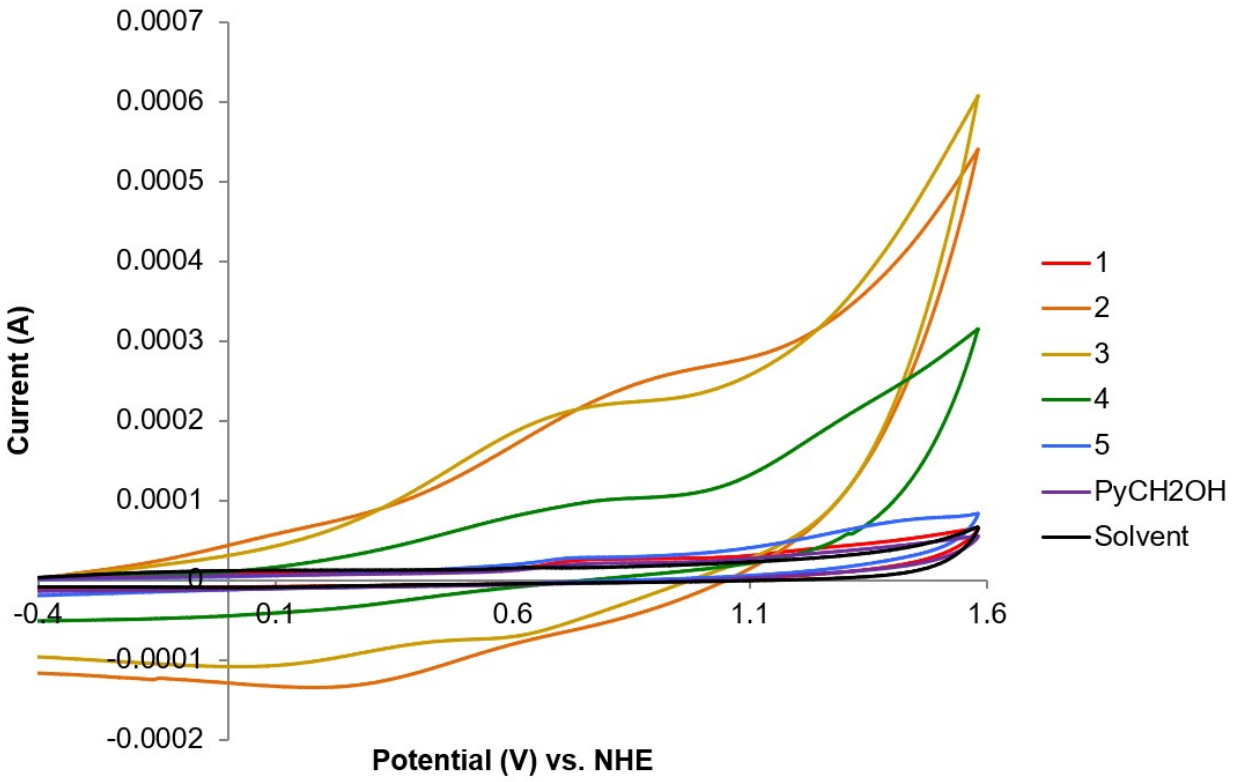
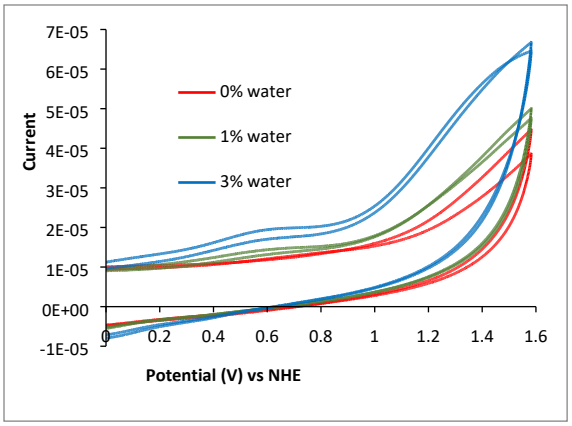
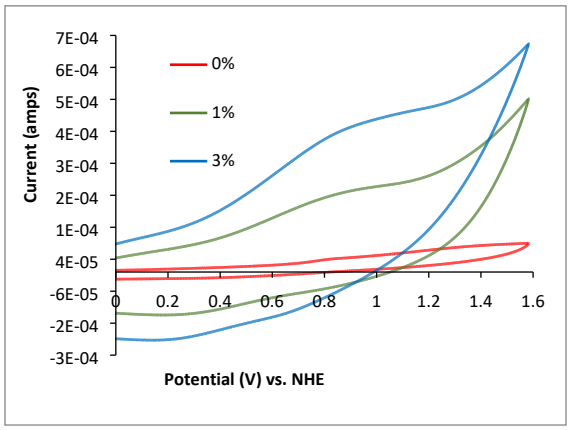


Figure S5. Cyclic voltammograms (1V/s) of electrocatalytic solvent decomposition containing compounds **1**-**5**, $PyCH_2OH$ (all at 1 mM) and baseline solvent/water mixture. All voltammograms (including "solvent") are in 1% water in propylene carbonate solution. The small impurity with a wave at 0.6 V is also decomposed by the catalyst based on the growth of this signal under catalytic conditions. Sweep range is from -1 to 1.6 V, though the topology of the voltammograms is the same when the scan is started from 0V.

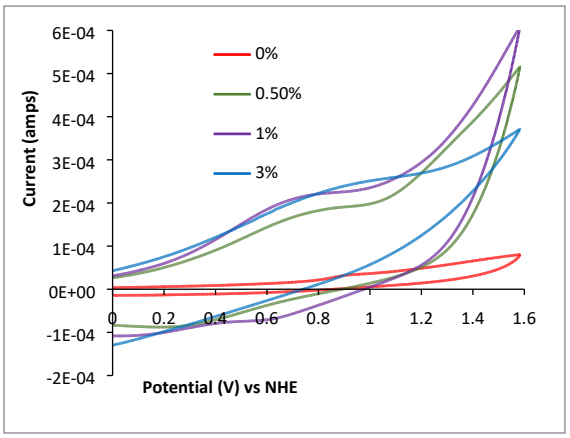
1.


7E-05
6E-05
5E-05
4E-05
3E-05
2E-05
1E-05
0E+00
-1E-05
Current
0% water
1% water
3% water
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
Potential (V) vs NHE

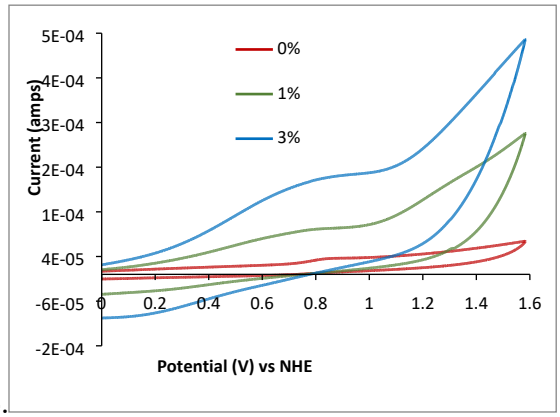
2.

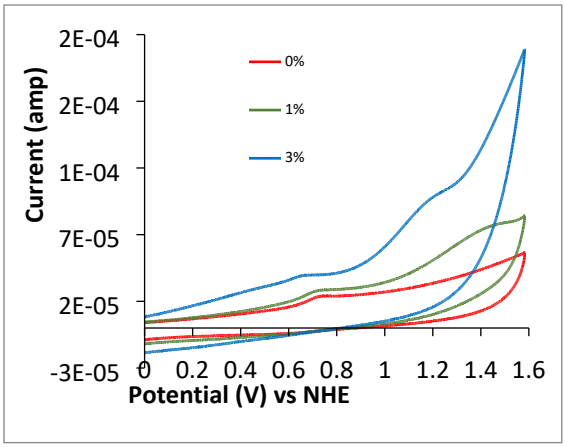

7E-04
6E-04
5E-04
4E-04
3E-04
2E-04
1E-04
4E-05
-6E-05
-2E-04
-3E-04
Current (amps)
0%
1%
3%
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
Potential (V) vs. NHE

3.


6E-04
5E-04
4E-04
3E-04
2E-04
1E-04
0E+00
-1E-04
-2E-04
Current (amps)
0%
0.50%
1%
3%
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
Potential (V) vs NHE

4.


5E-04
4E-04
3E-04
2E-04
1E-04
4E-05
-6E-05
-2E-04
Current (amps)
0%
1%
3%
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
Potential (V) vs NHE



5.

Figure S6. Cyclic voltammograms of hemicubane electrocatlysts **1** (500 mV/s) and **2-5** (1V/s) in the presence of variable-concentration water solutions in propylene carbonate electrolyte. The small impurity with a wave at 0.6 V is also decomposed by the catalyst based on the growth of this signal under catalytic conditions. Sweep range is from -1 to 1.6 V, though the topology of the voltammograms is the same when the scan is started from 0V.

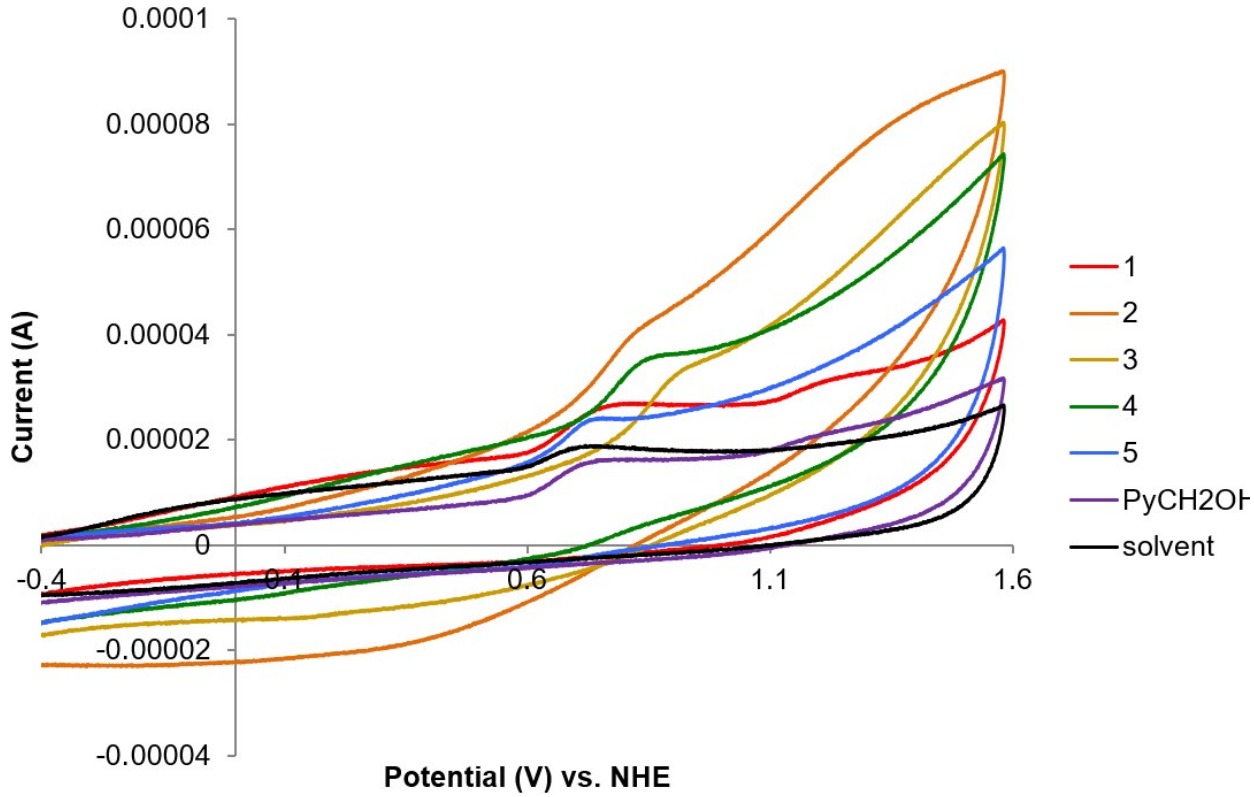


Figure S7. Cyclic voltammograms (1V/s) of Compounds **1-5**, $PyCH_2OH$, and solvent electrolyte under the same conditions as those in Figure 5 (main text), but in the absence of added water. The small impurity with a wave at 0.6 V is also decomposed by the catalyst based on the growth of this signal under catalytic conditions.

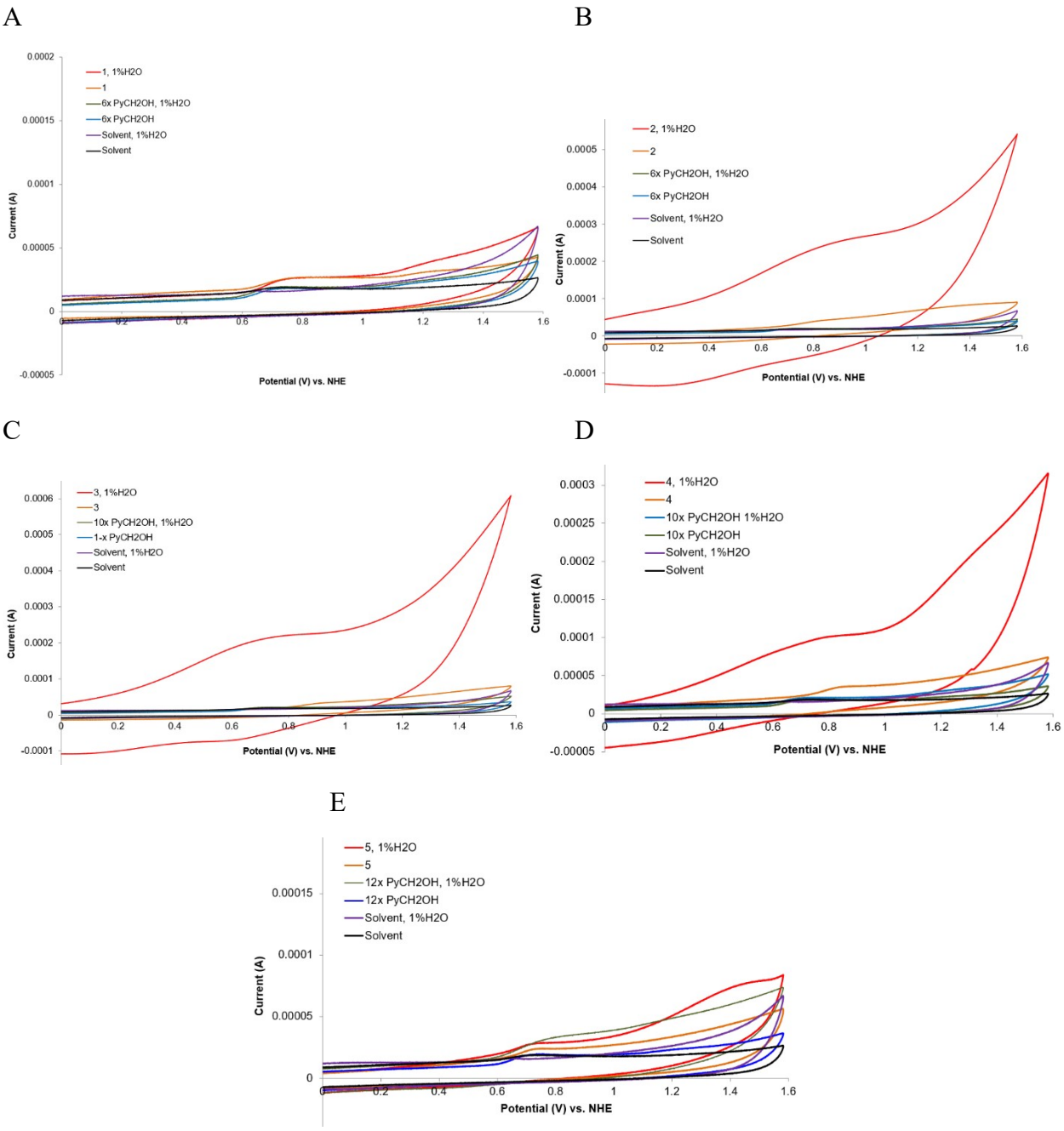


Figure S8. Cyclic voltammograms (1V/s) showing catalytic current of compounds **1-5** in comparison to equimolar scans in the absence of water, and to scans of equivalent ligand concentration in the presence and absence of water, and in comparison to scans in the absence of catalyst with and without water.

We considered the possibility that the ligand architecture alone might be responsible for the catalysis, and so we compared the electrocatalytic activity of propylene carbonate/water solutions with increased $PhCH_2OH$ concentrations such that we could measure catalytic current in solutions with constant ligand concentration while comparing unmetallated ligand to metallated ligand clusters. For example, Figure S8B shows the catalytic activity of $(CaMn_3(PyCH_2O)_6(NR_2)_2(THF))$ in comparison to a 6x-concentrated solution of $PyCH_2OH$ such that both solutions have the same $PyCH_2O$ content. In all cases except that of **1**, the catalytic activity of the cluster exceeded that of the ligand, suggesting the transition metal species is responsible for the catalytic current. The difference is most pronounced for compounds **2** and **3** (See Figure S8).

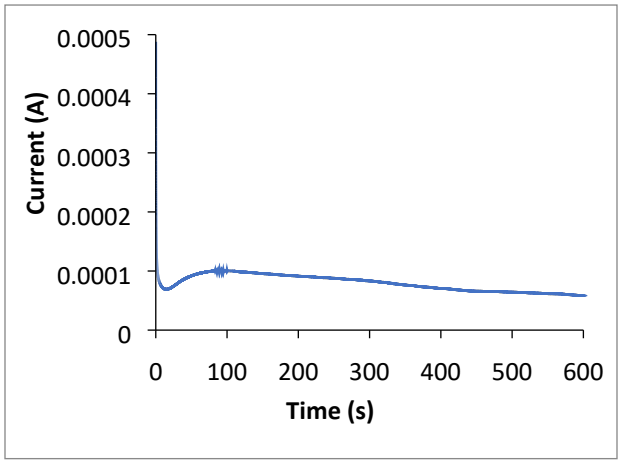
Compound **1** is the least effective catalyst, giving a similar current as a propylene carbonate-water mixture with no catalyst, and is less effective than the ligand alone (Figure S5, S8). This indicates that calcium ions in the cluster are essential to effect the catalytic transformation. Unlike previously reported electrocatalysis in this solvent mixture, we did not observe products of direct water oxidation (O_2, H_2O_2) based on GC analysis. Tests for H_2O_2 were performed by addition of MnO_2 to the reaction mixture following electrolysis to disproportionate any H_2O_2 into H_2O and O_2, but no O_2 was detected under these conditions either.

Examination of the voltammograms of **1**-**5** in 1% water solution in propylene carbonate (Figure S5) illustrates several key electrocatalytic observations. First, that calcium ions appear to be required for cooperative catalysis, as the CV of the all-Mn **1** shows very little activity above the uncatalyzed reaction (Figure S8) and poorer activity than free ligand. This is despite the water-accessible manganese termini in **1**, which feature both coordinative unsaturation, and a protolyzable NR_2 ligand which would be expected to be replaced by hydroxide via protolytic ligand exchange, extruding HNR_2. As such, water binding to manganese appears to be insufficient for electrocatalysis. Second, Ca:Mn ratios most similar to the biological OEC exhibited the best reactivity, with **2** and **3**—whose 1:3 and 1:5 Ca:Mn ratios are closest to 1:4 ratio of the OEC—being superior to **1**, **4**, and **5** (ratios 0:1, 1:2, and 4:3 respectively). Finally, the compound with the least structural analogy to the OEC, **5**, showed low activity (similar to **1**).

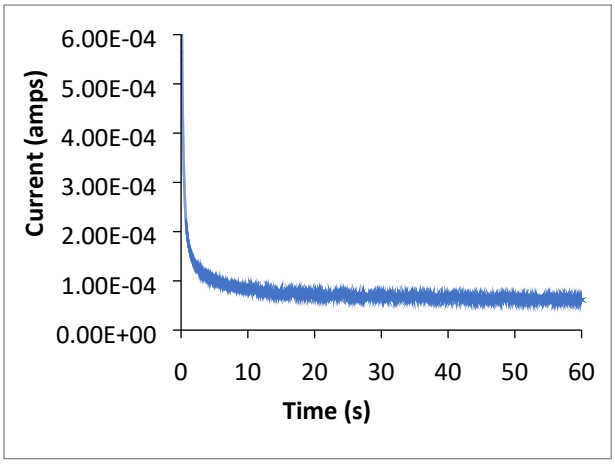
A common concern with any homogeneous electrocatalyst is the possible involvement of impurities in the catalysis, which could represent the active catalytic species. In particular, for self-assembled clusters with interchangeable components, such as in these systems, mixtures of clusters with different nuclearities are common. For instance, CHN analysis suggests that, while **2**,**3**, and **5** are pure, compounds **1**, and **4** may contain impurities. Alternatively, homogeneous catalyst precursors can decompose into solid-state or nanoparticulate catalysts at the electrode surface. A number of observations permit us to rule out contaminants as the active species in the observed electrocatalysis: 1) Measured catalytic current is similar from batch to batch (within 10%, most likely due to weighing error), which is not expected if small contaminants, (which can vary manyfold or even by an order of magnitude from batch to batch) are responsible for catalysis. 2). The best catalysts, **2** and **3**, also happen to be the among the purest samples based upon CHN combustion analysis, whereas the compounds that may be *contaminated* by other clusters (**1**, **4**) have lower activity. Compound **5** is a poor catalyst despite being pure based on

CHN analsysis. Indeed, if a contaminant cluster is responsible for catalysis in any of these samples, it is most likely that the electrocatalysis by the less pure (and less active) **4** is enhanced by contamination by the more active **2** or **3**, which may be present in small amounts due to their similar synthetic stoichiometry. 3) To determine whether these clusters serve as precatalysts for solid- or nanophase deposition at the electrode, we examined these catalysts by repeat scans and chronoamperometry, which should show a gradual increase in catalytic current if clusters deposit active catalyst at the electrode surface. Repeat scans on **4** do not result in a gradual increase in catalytic activity. Chronoamperometry generally show a steady catalytic current at about 1 x 10^{-4}A, after an initial Faradaic drop, with a steady but gradual decrease in catalytic current over time (Figure S9), which suggests a homogeneous, diffusion limited electrocatlytic reaction at the surface with gradual catalyst degradation, as opposed to the deposition of a homogeneous catalyst precursor to form active nanoparticulate or surface catalysts at the electrode. **2** does show a slight increase in current after the initial Faradaic drop, suggesting some deposition may occur at the electrode, but the similar current as observed in **3** and **4** suggests it also performs analogous homogeneous electrocatalysis as its primary mode of activity.

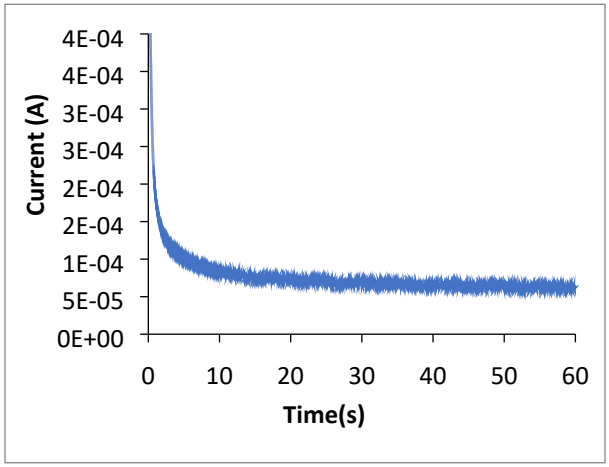
A



B



C



D

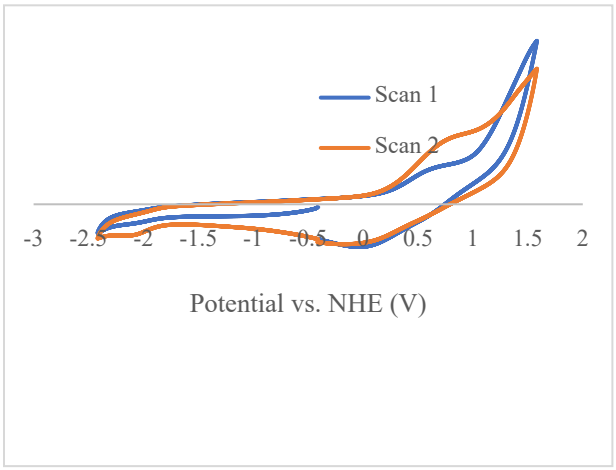


Figure S9. A: Chronoamperometry of **2** at 2V vs. NHE. B: Chronoamperometry of **3** at 2V vs. NHE. C: Chronoamperometry of **4** at 2V vs. NHE. After an initial spike of capacitive and Faradaic charging, current is steady at around 8 x 10^{-5} A, gradually decreasing over time. For catalyst **2**, a slight rise over the first minute may indicate catalyst deposition at the electrode. D: A repeat scan of catalyst **3** showing a decrease in current upon the 2nd scan.

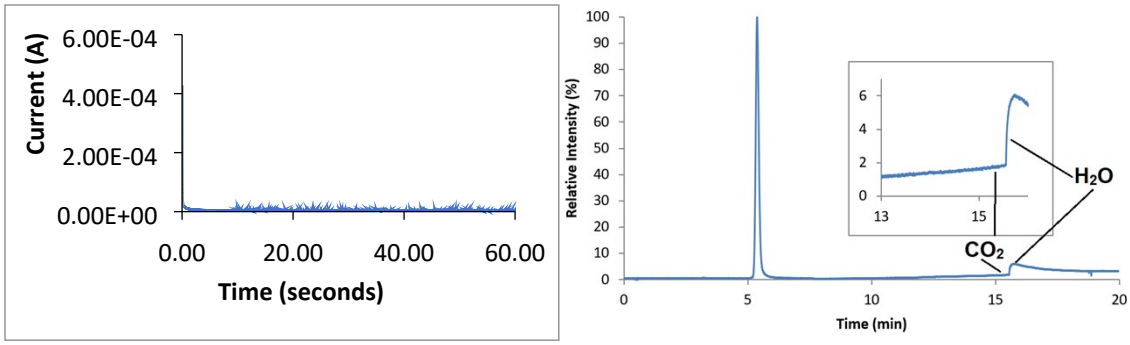


Figure S10. Chronoamperometry (left) on the lower-potential demonstrates the contaminant wave at 0.6 V vs. NHE (see Figures S5-S9) give short lived catalytic decomposition only lasting a few seconds, and no CO_2 formation, shown at right.

ATR-IR

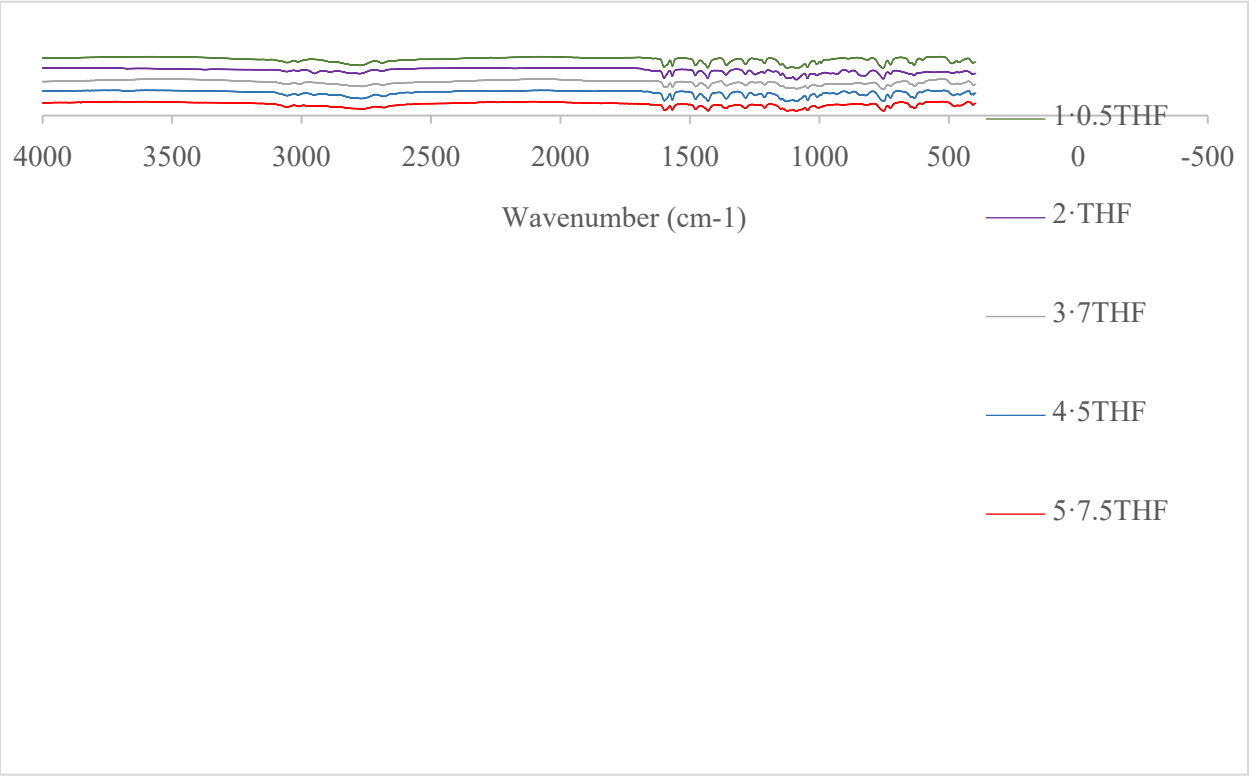


Figure S11. ATR-IR spectra of compounds **1-5**

X-Ray Crystallographic Tables

1·0.5 THF

Table S2 Crystal data and structure refinement for 1·0.5 THF

Empirical formula	$C_{26}H_{40}Mn_2N_4O_{3.5}Si_2$
Formula weight	630.68
Temperature/K	100.02
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.028(5)
b/Å	11.850(4)
c/Å	20.643(7)
α/°	90
β/°	93.358(7)
γ/°	90
Volume/Å^3	3181(2)
Z	4
ρ_{calc}g/cm^3	1.317
μ/mm^{-1}	0.902
F(000)	1320.0
Crystal size/mm^3	0.26 × 0.15 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.132 to 49.426
Index ranges	$-15 \le h \le 15$, $-13 \le k \le 13$, $0 \le l \le 24$
Reflections collected	5414
Independent reflections	5414 [R_{int} = ?, R_{sigma} = 0.0845]
Data/restraints/parameters	5414/166/408
Goodness-of-fit on F^2	1.107
Final R indexes [I>=2σ (I)]	R_1 = 0.0725, wR_2 = 0.1853
Final R indexes [all data]	R_1 = 0.1057, wR_2 = 0.2042
Largest diff. peak/hole / e Å^{-3}	0.92/-0.81

Table S3 Bond Lengths for 1·0.5 THF.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	O1	2.117(5)	N3	C17	1.348(8)
Mn1	O2[1]	2.142(4)	C1	C2	1.368(11)
Mn1	O4	2.153(5)	C2	C3	1.383(11)
Mn1	O4[1]	2.209(4)	C3	C4	1.377(11)
Mn1	N1	2.276(6)	C4	C5	1.373(10)
Mn1	N2[1]	2.282(6)	C5	C6	1.533(10)
Mn2	O1	2.111(5)	C7	C8	1.381(10)
Mn2	O2	2.064(4)	C8	C9	1.392(11)
Mn2	O4	2.257(4)	C9	C10	1.386(10)
Mn2	N3	2.320(6)	C10	C11	1.392(10)
Mn2	N4	2.113(5)	C11	C12	1.509(9)
Si1	N4	1.696(6)	C13	C14	1.376(11)
Si1	C19	1.885(8)	C14	C15	1.393(11)
Si1	C20	1.874(8)	C15	C16	1.374(10)
Si1	C21	1.878(8)	C16	C17	1.395(9)
Si2	N4	1.693(5)	C17	C18	1.499(9)
Si2	C22	1.882(7)	O1S	C1S	1.450(5)
Si2	C23	1.880(7)	O1S	C4S	1.451(5)
Si2	C24	1.877(8)	C1S	C3S	1.548(5)
O1	C6	1.371(8)	C2S	C3S	1.554(5)
O2	C12	1.399(8)	C2S	C4S	1.549(5)
O4	C18	1.403(7)	O1T	C1T	1.453(5)
N1	C1	1.336(9)	O1T	C4T	1.453(5)
N1	C5	1.343(8)	C1T	C3T	1.552(5)
N2	C7	1.342(9)	C2T	C3T	1.555(5)
N2	C11	1.342(8)	C2T	C4T	1.552(5)
N3	C13	1.341(9)			

[1]1-X,1-Y,1-Z

Table S4 Bond Angles for 1·0.5 THF.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Mn1	O2[1]	179.00(18)	C18	O4	Mn2	118.6(3)
O1	Mn1	O4[1]	99.67(17)	C1	N1	Mn1	126.5(5)
O1	Mn1	O4	78.63(17)	C1	N1	C5	118.7(6)
O1	Mn1	N1	74.78(18)	C5	N1	Mn1	114.7(4)
O1	Mn1	N2[1]	103.93(18)	C7	N2	Mn1[1]	127.2(5)
O2[1]	Mn1	O4[1]	81.14(16)	C11	N2	Mn1[1]	112.6(4)
O2[1]	Mn1	O4	100.93(17)	C11	N2	C7	119.6(6)
O2[1]	Mn1	N1	105.74(19)	C13	N3	Mn2	123.9(5)
O2[1]	Mn1	N2[1]	75.23(17)	C13	N3	C17	118.2(6)
O4	Mn1	O4[1]	82.44(17)	C17	N3	Mn2	117.9(4)
O4[1]	Mn1	N1	96.74(18)	Si1	N4	Mn2	116.1(3)
O4	Mn1	N1	152.88(19)	Si2	N4	Mn2	115.9(3)
O4[1]	Mn1	N2[1]	156.31(17)	Si2	N4	Si1	125.7(3)
O4	Mn1	N2[1]	100.21(18)	N1	C1	C2	122.8(7)
N1	Mn1	N2[1]	91.3(2)	C1	C2	C3	118.8(7)
O1	Mn2	O4	76.46(17)	C4	C3	C2	118.3(7)
O1	Mn2	N3	135.90(19)	C5	C4	C3	120.1(7)
O1	Mn2	N4	106.4(2)	N1	C5	C4	121.2(7)
O2	Mn2	O1	104.06(18)	N1	C5	C6	116.3(6)
O2	Mn2	O4	81.69(16)	C4	C5	C6	122.4(6)
O2	Mn2	N3	99.10(19)	O1	C6	C5	113.2(5)
O2	Mn2	N4	119.6(2)	N2	C7	C8	122.3(7)
O4	Mn2	N3	70.38(17)	C7	C8	C9	118.8(7)
N4	Mn2	O4	155.86(19)	C10	C9	C8	118.6(7)
N4	Mn2	N3	93.5(2)	C9	C10	C11	119.8(7)
N4	Si1	C19	110.6(3)	N2	C11	C10	120.8(6)
N4	Si1	C20	113.7(3)	N2	C11	C12	116.6(6)
N4	Si1	C21	113.6(3)	C10	C11	C12	122.6(6)
C20	Si1	C19	105.6(4)	O2	C12	C11	111.8(5)
C20	Si1	C21	106.7(3)	N3	C13	C14	123.5(7)
C21	Si1	C19	106.2(4)	C13	C14	C15	118.3(7)
N4	Si2	C22	116.2(3)	C16	C15	C14	118.7(7)
N4	Si2	C23	110.3(3)	C15	C16	C17	119.9(7)
N4	Si2	C24	110.6(3)	N3	C17	C16	121.3(6)
C23	Si2	C22	104.4(4)	N3	C17	C18	116.3(6)
C24	Si2	C22	105.3(4)	C16	C17	C18	122.4(6)
C24	Si2	C23	109.7(4)	O4	C18	C17	111.8(5)
Mn2	O1	Mn1	105.16(19)	C1S	O1S	C4S	106.8(7)
C6	O1	Mn1	120.8(4)	O1S	C1S	C3S	108.7(6)
C6	O1	Mn2	132.2(4)	C4S	C2S	C3S	104.8(5)

Mn2	O2	Mn1[1]	102.52(19)	C1S	C3S	C2S	104.2(5)
C12	O2	Mn1[1]	114.5(4)	O1S	C4S	C2S	108.3(6)
C12	O2	Mn2	134.3(4)	C1T	O1T	C4T	105.3(7)
Mn1	O4	Mn1[1]	97.56(17)	O1T	C1T	C3T	108.1(6)
Mn1	O4	Mn2	99.15(17)	C4T	C2T	C3T	103.9(5)
Mn1[1]	O4	Mn2	94.53(16)	C1T	C3T	C2T	104.2(5)
C18	O4	Mn1	123.5(4)	O1T	C4T	C2T	107.4(7)
C18	O4	Mn1[1]	117.8(4)				

[1]1-X,1-Y,1-Z

Experimental

A single crystal of $C_{26}H_{40}Mn_2N_4O_{3.5}Si_2$ was selected and mounted on a diffractometer. The crystal was kept at 100.02 K during data collection. The structure was solved with SHELXS structure solution program and refined with the SHELX refinement package using Least Squares minimisation.

Crystal structure determination of 1·0.5THF

Crystal Data for $C_{26}H_{40}Mn_2N_4O_{3.5}Si_2$ (M =630.68 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 13.028(5) Å, b = 11.850(4) Å, c = 20.643(7) Å, β = 93.358(7)°, V = 3181(2) Å^3, Z = 4, T = 100.02 K, μ(MoKα) = 0.902 mm^{-1}, *Dcalc* = 1.317 g/cm^3, 5414 reflections measured (3.132° ≤ 2Θ ≤ 49.426°), 5414 unique (R_{int} = ?, R_{sigma} = 0.0845) which were used in all calculations. The final R_1 was 0.0725 (I > 2σ(I)) and wR_2 was 0.2042 (all data).

Refinement model description

Number of restraints - 166, number of constraints - unknown.

Details:

1. Twinned data refinement
 Scales: 0.850(4)
 0.150(4)
2. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
3. Restrained distances
 C3S-C2S = C4S-C2S = C3S-C1S
 1.54 with sigma of 0.005
 C3T-C2T = C4T-C2T = C3T-C1T
 1.54 with sigma of 0.005
 O1S-C4S = O1S-C1S
 1.45 with sigma of 0.005
 O1T-C4T = O1T-C1T
 1.45 with sigma of 0.005
 C4S-C1S
 2.29 with sigma of 0.01
 C4T-C1T

2.29 with sigma of 0.01
O1S-C2S = O1S-C3S
2.44 with sigma of 0.01
O1T-C2T = O1T-C3T
2.44 with sigma of 0.01
C4S-C3S = C1S-C2S
2.51 with sigma of 0.01
C4T-C3T = C1T-C2T
2.51 with sigma of 0.01
4. Rigid bond restraints
O1S, O1S, C1S, C1S, C2S, C2S, C3S, C3S, C4S, C4S, O1T, O1T, C1T, C1T, C2T, C2T, C3T, C3T, C4T, C4T
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
5. Uiso/Uaniso restraints and constraints
O1S ≈ O1S ≈ C1S ≈ C1S ≈ C2S ≈ C2S ≈ C3S ≈ C3S ≈ C4S ≈ C4S ≈ O1T ≈ O1T ≈ C1T ≈ C1T ≈ C2T ≈ C2T ≈ C3T ≈ C3T ≈ C4T ≈ C4T: within 2A with sigma of 0.01 and sigma for terminal atoms of 0.02
6. Others
Sof(O1T)=Sof(C1T)=Sof(H1TA)=Sof(H1TB)=Sof(C2T)=Sof(H2TA)=Sof(H2TB)=Sof(C3T)=Sof(H3TA)=Sof(H3TB)=Sof(C4T)=Sof(H4TA)=Sof(H4TB)=0.5*(1-FVAR(2))
Sof(O1S)=Sof(C1S)=Sof(H1SA)=Sof(H1SB)=Sof(C2S)=Sof(H2SA)=Sof(H2SB)=Sof(C3S)=Sof(H3SA)=Sof(H3SB)=Sof(C4S)=Sof(H4SA)=Sof(H4SB)=0.5*FVAR(2)
7.a Secondary CH2 refined with riding coordinates:
C6(H6A,H6B), C12(H12A,H12B), C18(H18A,H18B), C1S(H1SA,H1SB), C2S(H2SA,H2SB), C3S(H3SA,H3SB), C4S(H4SA,H4SB), C1T(H1TA,H1TB), C2T(H2TA,H2TB), C3T(H3TA,H3TB), C4T(H4TA,H4TB)
7.b Me refined with riding coordinates:
C19(H19A,H19B,H19C), C20(H20A,H20B,H20C), C21(H21A,H21B,H21C), C22(H22A,H22B, H22C), C23(H23A,H23B,H23C), C24(H24A,H24B,H24C)
7.c Aromatic/amide H refined with riding coordinates:
C1(H1), C2(H2), C3(H3), C4(H4), C7(H7), C8(H8), C9(H9), C10(H10), C13(H13), C14(H14), C15(H15), C16(H16)
This report has been created with Olex2, compiled on 2018.05.29 svn.r3508 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

2·THF

Table S5 Crystal data and structure refinement for 2·THF.

Empirical formula	$C_{56}H_{88}CaMn_3N_8O_8Si_4$
Formula weight	1318.60
Temperature/K	100.06
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.5216(15)
b/Å	19.661(3)
c/Å	32.220(5)
α/°	90
β/°	93.239(3)
γ/°	90
Volume/Å^3	6654.7(17)
Z	4
ρ_{calc}g/cm^3	1.316
μ/mm^{-1}	0.764
F(000)	2780.0
Crystal size/mm^3	0.55 × 0.42 × 0.4
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.472 to 55.942
Index ranges	$-13 \leq h \leq 13$, $-25 \leq k \leq 25$, $-42 \leq l \leq 42$
Reflections collected	110437
Independent reflections	15931 [R_{int} = 0.0295, R_{sigma} = 0.0177]
Data/restraints/parameters	15931/204/779
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0332, wR_2 = 0.0794
Final R indexes [all data]	R_1 = 0.0410, wR_2 = 0.0848
Largest diff. peak/hole / e Å^{-3}	1.06/-0.50

Table S6 Bond Lengths for 2·THF

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	O1	2.1183(12)	N2	C11	1.336(2)
Mn1	O2	2.1197(12)	N3	C13	1.334(3)
Mn1	O3	2.1683(12)	N3	C18	1.335(3)
Mn1	O4	2.1852(11)	N4	C19	1.342(2)
Mn1	N1	2.2984(15)	N4	C23	1.342(2)
Mn1	N2	2.2842(15)	N5	C25	1.344(2)
Mn2	Ca1	3.4614(6)	N5	C29	1.331(3)
Mn2	O2	2.0891(12)	N6	C31	1.350(3)
Mn2	O3	2.2046(12)	N6	C35	1.319(3)
Mn2	O5	2.1188(12)	C0AA	C18	1.504(3)
Mn2	N5	2.2968(15)	C1	C2	1.373(3)
Mn2	N7	2.1039(14)	C2	C3	1.387(4)
Mn3	Ca1	3.4564(6)	C3	C4	1.374(3)
Mn3	O1	2.0762(12)	C4	C5	1.389(3)
Mn3	O4	2.2178(12)	C5	C6	1.510(2)
Mn3	O6	2.1083(13)	C7	C8	1.379(3)
Mn3	N6	2.3072(16)	C8	C9	1.390(3)
Mn3	N8	2.0911(15)	C9	C10	1.376(3)
Ca1	O3	2.3707(12)	C10	C11	1.392(2)
Ca1	O4	2.3875(12)	C11	C12	1.514(2)
Ca1	O5	2.2855(13)	C13	C14	1.387(3)
Ca1	O6	2.2813(13)	C14	C15	1.367(4)
Ca1	O7	2.4634(14)	C15	C16	1.381(3)
Ca1	N3	2.6551(17)	C16	C18	1.393(3)
Ca1	N4	2.6326(16)	C19	C20	1.385(3)
Si1	N7	1.6970(15)	C20	C21	1.380(3)
Si1	C37	1.871(2)	C21	C22	1.384(3)
Si1	C38	1.885(2)	C22	C23	1.396(2)
Si1	C39	1.884(2)	C23	C24	1.510(2)
Si2	N7	1.6976(15)	C25	C26	1.377(3)
Si2	C40	1.8863(18)	C26	C27	1.378(4)
Si2	C41	1.880(2)	C27	C28	1.380(3)
Si2	C42	1.883(2)	C28	C29	1.393(3)
Si3	N8	1.6987(15)	C29	C30	1.519(3)
Si3	C43	1.871(2)	C31	C32	1.376(3)
Si3	C44	1.887(2)	C32	C33	1.366(4)
Si3	C45	1.884(2)	C33	C34	1.381(4)
Si4	N8	1.6880(16)	C34	C35	1.400(3)
Si4	C46	1.893(2)	C35	C36	1.519(3)
Si4	C47	1.8811(19)	C49	C50	1.509(3)

Si4	C48	1.881(2)	C50	C51	1.471(4)
O1	C6	1.381(2)	C51	C52	1.508(3)
O2	C12	1.380(2)	O1S	C1S	1.478(5)
O3	C0AA	1.402(2)	O1S	C4S	1.492(5)
O4	C24	1.403(2)	C1S	C2S	1.508(5)
O5	C30	1.379(2)	C2S	C3S	1.496(5)
O6	C36	1.385(2)	C3S	C4S	1.502(5)
O7	C49	1.446(2)	O1T	C1T	1.488(4)
O7	C52	1.446(3)	O1T	C4T	1.476(4)
N1	C1	1.342(2)	C1T	C2T	1.499(4)
N1	C5	1.337(2)	C2T	C3T	1.492(4)
N2	C7	1.342(2)	C3T	C4T	1.474(4)

Table S7 Bond Angles for 2·THF.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Mn1	O2	172.42(5)	Mn1	O4	Mn3	97.21(4)
O1	Mn1	O3	102.26(5)	Mn1	O4	Ca1	98.97(4)
O1	Mn1	O4	78.99(4)	Mn3	O4	Ca1	97.20(4)
O1	Mn1	N1	73.17(5)	C24	O4	Mn1	119.43(10)
O1	Mn1	N2	105.88(5)	C24	O4	Mn3	124.21(10)
O2	Mn1	O3	78.79(4)	C24	O4	Ca1	114.85(10)
O2	Mn1	O4	108.59(5)	Mn2	O5	Ca1	103.55(5)
O2	Mn1	N1	99.26(5)	C30	O5	Mn2	119.89(11)
O2	Mn1	N2	74.04(5)	C30	O5	Ca1	135.19(11)
O3	Mn1	O4	84.83(4)	Mn3	O6	Ca1	103.82(5)
O3	Mn1	N1	97.75(5)	C36	O6	Mn3	119.47(12)
O3	Mn1	N2	151.34(5)	C36	O6	Ca1	135.87(12)
O4	Mn1	N1	151.96(5)	C49	O7	Ca1	127.95(12)
O4	Mn1	N2	95.20(5)	C52	O7	Ca1	122.11(12)
N2	Mn1	N1	95.47(5)	C52	O7	C49	109.86(15)
O2	Mn2	Ca1	95.00(3)	C1	N1	Mn1	127.01(13)
O2	Mn2	O3	78.62(4)	C5	N1	Mn1	114.28(11)
O2	Mn2	O5	106.23(5)	C5	N1	C1	118.23(17)
O2	Mn2	N5	92.93(5)	C7	N2	Mn1	126.86(12)
O2	Mn2	N7	122.39(5)	C11	N2	Mn1	114.55(11)
O3	Mn2	Ca1	42.67(3)	C11	N2	C7	118.56(15)
O3	Mn2	N5	152.52(5)	C13	N3	Ca1	129.38(15)
O5	Mn2	Ca1	39.93(3)	C13	N3	C18	117.44(18)
O5	Mn2	O3	82.56(5)	C18	N3	Ca1	112.32(12)
O5	Mn2	N5	74.72(5)	C19	N4	Ca1	128.43(12)
N5	Mn2	Ca1	113.61(4)	C23	N4	Ca1	112.71(11)
N7	Mn2	Ca1	131.21(4)	C23	N4	C19	117.49(15)
N7	Mn2	O3	110.68(5)	C25	N5	Mn2	126.61(14)
N7	Mn2	O5	131.03(5)	C29	N5	Mn2	113.99(12)
N7	Mn2	N5	95.99(6)	C29	N5	C25	118.60(17)
O1	Mn3	Ca1	93.10(4)	C31	N6	Mn3	126.66(15)
O1	Mn3	O4	79.14(4)	C35	N6	Mn3	113.10(13)
O1	Mn3	O6	108.44(5)	C35	N6	C31	119.03(18)
O1	Mn3	N6	94.15(5)	Si1	N7	Mn2	115.37(8)
O1	Mn3	N8	119.26(6)	Si1	N7	Si2	125.00(8)
O4	Mn3	Ca1	43.26(3)	Si2	N7	Mn2	119.29(8)
O4	Mn3	N6	153.39(5)	Si3	N8	Mn3	115.87(8)
O6	Mn3	Ca1	39.86(3)	Si4	N8	Mn3	122.00(8)
O6	Mn3	O4	82.98(5)	Si4	N8	Si3	122.02(9)
O6	Mn3	N6	74.71(6)	O3	C0AA	C18	111.71(15)

N6	Mn3	Ca1	112.52(5)	N1	C1	C2	123.0(2)
N8	Mn3	Ca1	136.77(4)	C1	C2	C3	118.4(2)
N8	Mn3	O4	111.72(5)	C4	C3	C2	119.2(2)
N8	Mn3	O6	131.72(5)	C3	C4	C5	118.9(2)
N8	Mn3	N6	94.10(6)	N1	C5	C4	122.17(17)
O3	Ca1	O4	76.21(4)	N1	C5	C6	116.76(15)
O3	Ca1	O7	140.72(5)	C4	C5	C6	121.06(17)
O3	Ca1	N3	66.05(5)	O1	C6	C5	112.18(14)
O3	Ca1	N4	137.84(4)	N2	C7	C8	122.92(16)
O4	Ca1	O7	143.07(5)	C7	C8	C9	118.48(17)
O4	Ca1	N3	136.31(5)	C10	C9	C8	118.80(17)
O4	Ca1	N4	66.73(4)	C9	C10	C11	119.42(17)
O5	Ca1	O3	75.55(4)	N2	C11	C10	121.82(16)
O5	Ca1	O4	94.78(4)	N2	C11	C12	116.93(14)
O5	Ca1	O7	95.74(5)	C10	C11	C12	121.25(15)
O5	Ca1	N3	96.30(5)	O2	C12	C11	112.25(14)
O5	Ca1	N4	87.89(5)	N3	C13	C14	123.6(2)
O6	Ca1	O3	96.93(4)	C15	C14	C13	118.6(2)
O6	Ca1	O4	75.74(4)	C14	C15	C16	118.86(19)
O6	Ca1	O5	169.24(5)	C15	C16	C18	119.1(2)
O6	Ca1	O7	94.93(5)	N3	C18	C0AA	115.97(16)
O6	Ca1	N3	87.42(5)	N3	C18	C16	122.41(18)
O6	Ca1	N4	92.89(5)	C16	C18	C0AA	121.62(19)
O7	Ca1	N3	77.27(5)	N4	C19	C20	123.80(18)
O7	Ca1	N4	78.41(5)	C21	C20	C19	118.33(17)
N4	Ca1	N3	155.61(5)	C20	C21	C22	118.96(17)
N7	Si1	C37	112.46(8)	C21	C22	C23	119.11(18)
N7	Si1	C38	114.08(9)	N4	C23	C22	122.32(16)
N7	Si1	C39	114.00(9)	N4	C23	C24	116.37(15)
C37	Si1	C38	104.56(10)	C22	C23	C24	121.31(16)
C37	Si1	C39	104.80(11)	O4	C24	C23	112.07(14)
C39	Si1	C38	106.03(9)	N5	C25	C26	123.0(2)
N7	Si2	C40	115.21(8)	C25	C26	C27	118.4(2)
N7	Si2	C41	111.46(8)	C26	C27	C28	119.0(2)
N7	Si2	C42	114.67(9)	C27	C28	C29	119.4(2)
C41	Si2	C40	104.87(9)	N5	C29	C28	121.54(19)
C41	Si2	C42	106.63(10)	N5	C29	C30	116.51(16)
C42	Si2	C40	103.06(10)	C28	C29	C30	121.95(19)
N8	Si3	C43	111.73(8)	O5	C30	C29	114.03(16)
N8	Si3	C44	112.73(8)	N6	C31	C32	123.3(2)
N8	Si3	C45	112.99(9)	C33	C32	C31	117.7(2)
C43	Si3	C44	106.04(9)	C32	C33	C34	119.7(2)

C43	Si3	C45	104.59(10)	C33	C34	C35	119.4(2)
C45	Si3	C44	108.20(9)	N6	C35	C34	120.8(2)
N8	Si4	C46	114.30(10)	N6	C35	C36	117.18(17)
N8	Si4	C47	112.51(8)	C34	C35	C36	122.1(2)
N8	Si4	C48	111.92(9)	O6	C36	C35	113.81(17)
C47	Si4	C46	104.04(9)	O7	C49	C50	105.14(18)
C48	Si4	C46	105.99(11)	C51	C50	C49	104.4(2)
C48	Si4	C47	107.47(9)	C50	C51	C52	104.1(2)
Mn3	O1	Mn1	103.90(5)	O7	C52	C51	105.60(19)
C6	O1	Mn1	120.80(10)	C1S	O1S	C4S	106.2(4)
C6	O1	Mn3	128.83(11)	O1S	C1S	C2S	105.7(5)
Mn2	O2	Mn1	103.19(5)	C3S	C2S	C1S	106.8(5)
C12	O2	Mn1	120.44(10)	C2S	C3S	C4S	106.0(4)
C12	O2	Mn2	127.76(11)	O1S	C4S	C3S	108.2(4)
Mn1	O3	Mn2	97.91(4)	C4T	O1T	C1T	106.3(4)
Mn1	O3	Ca1	99.97(5)	O1T	C1T	C2T	107.7(4)
Mn2	O3	Ca1	98.26(5)	C3T	C2T	C1T	108.5(4)
C0AA	O3	Mn1	117.55(10)	C4T	C3T	C2T	105.9(4)
C0AA	O3	Mn2	124.04(10)	C3T	C4T	O1T	111.0(4)
C0AA	O3	Ca1	114.79(10)				

Experimental

Aingle crystal of $C_{56}H_{88}CaMn_3N_8O_8Si_4$ was selected and mounted on a diffractometer. The crystal was kept at 100.06 K during data collectionThe structure was solved with the SHELXS structure solution program and refined with the SHELX refinement package using Least Squares minimization using OLEX2 [1] as a GUI.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

Crystal structure determination of 1·THF

Crystal Data for $C_{56}H_{88}CaMn_3N_8O_8Si_4$ (M =1318.60 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 10.5216(15) Å, b = 19.661(3) Å, c = 32.220(5) Å, β = 93.239(3)°, V = 6654.7(17) Å^3, Z = 4, T = 100.06 K, μ(MoKα) = 0.764 mm^{-1}, $Dcalc$ = 1.316 g/cm^3, 110437 reflections measured (5.472° ≤ 2Θ ≤ 55.942°), 15931 unique (R_{int} = 0.0295, R_{sigma} = 0.0177) which were used in all calculations. The final R_1 was 0.0332 (I > 2σ(I)) and wR_2 was 0.0848 (all data).

Refinement model description

Number of restraints - 204, number of constraints - unknown.
Details:
1. Fixed Uiso
At 1.2 times of:
All C(H) groups, All C(H,H) groups

At 1.5 times of:
All C(H,H,H) groups
2. Restrained distances
C2T-C1T = O1S-C1S = O1T-C1T = C4T-O1T = C4S-O1S = C2S-C3S = C2T-C3T = C3S-C4S = C3T-C4T = C2S-C1S
1.5 with sigma of 0.005
O1S-C1S = O1S-C4S = O1T-C1T = O1T-C4T
1.45 with sigma of 0.02
C2S-C1S = C3S-C2S = C4S-C3S = C2T-C1T = C3T-C2T = C4T-C3T
1.54 with sigma of 0.02
O1T-C2T = O1S-C2S = C1T-C4T = C1T-C3T = C1S-C4S = C1S-C3S = O1T-C3T = C2T-C4T = C2S-C4S = O1S-C3S
2.4 with sigma of 0.01
C1S-C4S
2.29 with sigma of 0.04
C1T-C4T
2.29 with sigma of 0.04
O1S-C2S
2.44 with sigma of 0.04
O1S-C3S
2.44 with sigma of 0.04
O1T-C2T
2.44 with sigma of 0.04
O1T-C3T
2.44 with sigma of 0.04
C1S-C3S
2.51 with sigma of 0.04
C4S-C2S
2.51 with sigma of 0.04
C1T-C3T
2.51 with sigma of 0.04
C2T-C4T
2.51 with sigma of 0.04
3. Rigid bond restraints
O1S, C1S, C2S, C3S, C4S, O1T, C1T, C2T, C3T, C4T
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
4. Uiso/Uaniso restraints and constraints
O1S ≈ C1S ≈ C2S ≈ C3S ≈ C4S ≈ O1T ≈ C1T ≈ C2T ≈
C3T ≈ C4T: within 2A with sigma of 0.04 and sigma for terminal atoms of 0.08
5. Others
Sof(O1S)=Sof(C1S)=Sof(H1SA)=Sof(H1SB)=Sof(C2S)=Sof(H2SA)=Sof(H2SB)=Sof(C3S)=
Sof(H3SA)=Sof(H3SB)=Sof(C4S)=Sof(H4SA)=Sof(H4SB)=1-FVAR(1)
Sof(O1T)=Sof(C1T)=Sof(H1TA)=Sof(H1TB)=Sof(C2T)=Sof(H2TA)=Sof(H2TB)=Sof(C3T)=
Sof(H3TA)=Sof(H3TB)=Sof(C4T)=Sof(H4TA)=Sof(H4TB)=FVAR(1)
6.a Secondary CH2 refined with riding coordinates:
C0AA(H0AA,H0AB), C6(H6A,H6B), C12(H12A,H12B), C24(H24B,H24A),

C30(H30A,H30B),
C36(H36A,H36B), C49(H49A,H49B), C50(H50A,H50B), C51(H51A,H51B),
C52(H52A,H52B),
C1S(H1SA,H1SB), C2S(H2SA,H2SB), C3S(H3SA,H3SB), C4S(H4SA,H4SB), C1T(H1TA,
H1TB), C2T(H2TA,H2TB), C3T(H3TA,H3TB), C4T(H4TA,H4TB)
6.b Aromatic/amide H refined with riding coordinates:
C1(H1), C2(H2), C3(H3), C4(H4), C7(H7), C8(H8), C9(H9), C10(H10), C13(H13),
C14(H14), C15(H15), C16(H16), C19(H19), C20(H20), C21(H21), C22(H22), C25(H25),
C26(H26), C27(H27), C28(H28), C31(H31), C32(H32), C33(H33), C34(H34)
6.c Idealised Me refined as rotating group:
C37(H37A,H37B,H37C), C38(H38A,H38B,H38C), C39(H39A,H39B,H39C),
C40(H40A,H40B,
H40C), C41(H41A,H41B,H41C), C42(H42A,H42B,H42C), C43(H43A,H43B,H43C),
C44(H44A,
H44B,H44C), C45(H45A,H45B,H45C), C46(H46A,H46B,H46C), C47(H47A,H47B,H47C),
C48(H48A,H48B,H48C)
This report has been created with Olex2, compiled on 2018.05.29 svn.r3508 for OlexSys.
Please let us know if there are any errors or if you would like to have additional features.

3·2THF

Table S8 Crystal data and structure refinement for 3·2THF.

Empirical formula	$C_{80}H_{112}CaMn_5N_{12}O_{12}Si_4$
Formula weight	1860.95
Temperature/K	100.03
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.598(4)
b/Å	16.828(4)
c/Å	43.150(11)
α/°	90
β/°	91.079(5)
γ/°	90
Volume/Å^3	11324(5)
Z	4
ρ_{calc}g/cm^3	1.092
μ/mm^{-1}	0.680
F(000)	3892.0
Crystal size/mm^3	0.5 × 0.28 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.07 to 41.872
Index ranges	$-15 \le h \le 15$, $-16 \le k \le 16$, $-43 \le l \le 43$
Reflections collected	50837
Independent reflections	11966 [R_{int} = 0.1078, R_{sigma} = 0.0938]
Data/restraints/parameters	11966/730/1195
Goodness-of-fit on F^2	1.009
Final R indexes [I>=2σ (I)]	R_1 = 0.0679, wR_2 = 0.1652
Final R indexes [all data]	R_1 = 0.1111, wR_2 = 0.1896
Largest diff. peak/hole / e Å^{-3}	0.98/-0.57

Table S9 Bond Lengths for 3·2THF.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	Ca1	3.519(2)	N4	C23	1.347(10)
Mn1	O1	2.156(6)	N5	C25	1.354(10)
Mn1	O2	2.180(6)	N5	C29	1.349(10)
Mn1	O5	2.163(5)	N6	C31	1.354(10)
Mn1	O9	2.154(5)	N6	C35	1.320(10)
Mn1	N1	2.287(7)	N7	C37	1.338(14)
Mn1	N2	2.302(7)	N7	C41	1.341(14)
Mn2	Ca1	3.560(2)	N8	C43	1.336(10)
Mn2	O3	2.176(5)	N8	C47	1.324(10)

Mn2	O6	2.166(5)	N9	C49	1.346(11)
Mn2	O7	2.109(5)	N9	C53	1.333(10)
Mn2	O8	2.188(5)	N10	C55	1.336(11)
Mn2	N6	2.300(6)	N10	C59	1.336(11)
Mn2	N7	2.263(13)	C1	C2	1.379(13)
Mn2	N7A	2.290(14)	C1S	C2S	1.53(2)
Mn3	Ca1	3.641(2)	C1T	C2T	1.515(18)
Mn3	O1	2.098(5)	C2	C3	1.374(13)
Mn3	O3	2.178(5)	C2S	C3S	1.56(2)
Mn3	O5	2.269(5)	C2T	C3T	1.544(18)
Mn3	O8	2.265(5)	C3	C4	1.335(12)
Mn3	O10	2.126(6)	C3S	C4S	1.54(2)
Mn3	N8	2.294(6)	C3T	C4T	1.524(18)
Mn4	Ca1	3.608(2)	C4	C5	1.409(12)
Mn4	O2	2.093(5)	C5	C6	1.495(12)
Mn4	O4	2.072(5)	C5S	C6S	1.607(17)
Mn4	O9	2.239(5)	C5T	C6T	1.57(2)
Mn4	N9	2.294(7)	C6S	C7S	1.544(16)
Mn4	N11	2.157(7)	C6T	C7T	1.54(2)
Mn5	O6	2.091(5)	C7	C8	1.412(14)
Mn5	O8	2.228(5)	C7S	C8S	1.519(16)
Mn5	O10	2.112(5)	C7T	C8T	1.55(2)
Mn5	N10	2.327(7)	C8	C9	1.333(14)
Mn5	N12	2.114(7)	C9	C10	1.381(13)
Ca1	O3	2.448(5)	C10	C11	1.407(12)
Ca1	O4	2.358(5)	C11	C12	1.505(12)
Ca1	O5	2.440(5)	C13	C14	1.377(12)
Ca1	O7	2.393(5)	C14	C15	1.360(12)
Ca1	O9	2.580(5)	C15	C16	1.391(12)
Ca1	N3	2.611(6)	C16	C17	1.392(12)
Ca1	N4	2.671(7)	C17	C18	1.525(10)
Ca1	N5	2.633(7)	C19	C20	1.411(12)
Si1	N11	1.715(7)	C20	C21	1.378(13)
Si1	C61	1.870(10)	C21	C22	1.362(13)
Si1	C62	1.885(9)	C22	C23	1.403(11)
Si1	C63	1.900(10)	C23	C24	1.493(11)
Si2	N11	1.668(7)	C25	C26	1.359(12)
Si2	C64	1.894(9)	C26	C27	1.379(12)
Si2	C65	1.869(11)	C27	C28	1.364(12)
Si2	C66	1.886(11)	C28	C29	1.391(11)
Si3	N12	1.699(7)	C29	C30	1.500(11)
Si3	C67	1.884(9)	C31	C32	1.360(11)

Si3	C68	1.895(10)	C32	C33	1.371(12)
Si3	C69	1.868(11)	C33	C34	1.384(11)
Si4	N12	1.703(8)	C34	C35	1.409(11)
Si4	C70	1.897(9)	C35	C36	1.511(11)
Si4	C71	1.876(9)	C37	C38	1.379(15)
Si4	C72	1.878(10)	C38	C39	1.373(15)
O1	C6	1.391(9)	C39	C40	1.398(15)
O1S	C1S	1.47(2)	C40	C41	1.377(15)
O1S	C4S	1.46(2)	C41	C42	1.509(15)
O1T	C1T	1.524(17)	C43	C44	1.377(11)
O1T	C4T	1.464(17)	C44	C45	1.382(12)
O2	C12	1.371(10)	C45	C46	1.358(12)
O2S	C5S	1.434(16)	C46	C47	1.407(11)
O2S	C8S	1.435(15)	C47	C48	1.509(11)
O2T	C5T	1.45(2)	C49	C50	1.391(13)
O2T	C8T	1.47(2)	C50	C51	1.375(13)
O3	C18	1.404(8)	C51	C52	1.374(13)
O4	C24	1.389(9)	C52	C53	1.373(11)
O5	C30	1.414(9)	C53	C54	1.504(11)
O6	C36	1.382(9)	C55	C56	1.383(13)
O7	C42	1.418(14)	C56	C57	1.376(14)
O7	C42A	1.415(16)	C57	C58	1.375(14)
O8	C48	1.411(9)	C58	C59	1.409(12)
O9	C54	1.398(9)	C59	C60	1.512(12)
O10	C60	1.375(9)	C37A	C38A	1.386(16)
N1	C1	1.367(11)	C37A	N7A	1.336(16)
N1	C5	1.343(11)	C38A	C39A	1.377(16)
N2	C7	1.369(11)	N7A	C41A	1.345(15)
N2	C11	1.350(11)	C42A	C41A	1.512(16)
N3	C13	1.354(10)	C40A	C39A	1.383(16)
N3	C17	1.341(10)	C40A	C41A	1.392(16)
N4	C19	1.330(11)			

Table S10 Bond Angles for final.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Mn1	Ca1	97.42(14)	C30	O5	Mn3	117.0(4)
O1	Mn1	O2	171.2(2)	C30	O5	Ca1	115.1(4)
O1	Mn1	O5	79.03(19)	Mn5	O6	Mn2	101.8(2)
O1	Mn1	N1	72.3(2)	C36	O6	Mn2	120.4(4)
O1	Mn1	N2	112.5(3)	C36	O6	Mn5	130.6(5)
O2	Mn1	Ca1	85.38(14)	Mn2	O7	Ca1	104.3(2)
O2	Mn1	N1	100.7(3)	C42	O7	Mn2	112.0(9)
O2	Mn1	N2	72.1(3)	C42	O7	Ca1	141.5(9)
O5	Mn1	Ca1	43.13(13)	C42A	O7	Mn2	123.1(11)
O5	Mn1	O2	108.3(2)	C42A	O7	Ca1	128.5(10)
O5	Mn1	N1	150.7(3)	Mn2	O8	Mn3	94.64(19)
O5	Mn1	N2	97.1(2)	Mn2	O8	Mn5	96.9(2)
O9	Mn1	Ca1	46.85(14)	Mn5	O8	Mn3	97.40(19)
O9	Mn1	O1	96.0(2)	C48	O8	Mn2	129.4(4)
O9	Mn1	O2	79.8(2)	C48	O8	Mn3	115.3(4)
O9	Mn1	O5	87.59(19)	C48	O8	Mn5	116.8(4)
O9	Mn1	N1	101.1(2)	Mn1	O9	Mn4	98.2(2)
O9	Mn1	N2	151.5(3)	Mn1	O9	Ca1	95.62(19)
N1	Mn1	Ca1	146.21(17)	Mn4	O9	Ca1	96.69(18)
N1	Mn1	N2	88.5(2)	C54	O9	Mn1	114.3(4)
N2	Mn1	Ca1	124.60(19)	C54	O9	Mn4	113.7(5)
O3	Mn2	Ca1	42.54(13)	C54	O9	Ca1	132.2(4)
O3	Mn2	O8	84.50(18)	Mn5	O10	Mn3	105.6(2)
O3	Mn2	N6	96.3(2)	C60	O10	Mn3	131.2(5)
O3	Mn2	N7	160.7(5)	C60	O10	Mn5	120.9(5)
O3	Mn2	N7A	153.4(6)	C1	N1	Mn1	124.2(7)
O6	Mn2	Ca1	142.45(15)	C5	N1	Mn1	117.1(6)
O6	Mn2	O3	100.85(19)	C5	N1	C1	118.7(8)
O6	Mn2	O8	79.31(19)	C7	N2	Mn1	127.4(7)
O6	Mn2	N6	72.9(2)	C11	N2	Mn1	114.4(5)
O6	Mn2	N7	97.5(5)	C11	N2	C7	118.1(8)
O6	Mn2	N7A	104.9(6)	C13	N3	Ca1	124.5(6)
O7	Mn2	Ca1	40.65(13)	C17	N3	Ca1	117.6(5)
O7	Mn2	O3	82.79(19)	C17	N3	C13	117.4(7)
O7	Mn2	O6	175.17(19)	C19	N4	Ca1	124.8(6)
O7	Mn2	O8	104.3(2)	C19	N4	C23	118.6(7)
O7	Mn2	N6	103.7(2)	C23	N4	Ca1	116.3(5)
O7	Mn2	N7	79.2(5)	C25	N5	Ca1	128.1(5)
O7	Mn2	N7A	71.9(6)	C29	N5	Ca1	115.0(5)
O8	Mn2	Ca1	100.39(14)	C29	N5	C25	116.6(7)

O8	Mn2	N6	151.8(2)	C31	N6	Mn2	125.7(6)
O8	Mn2	N7	93.2(7)	C35	N6	Mn2	115.0(5)
O8	Mn2	N7A	93.9(8)	C35	N6	C31	118.9(7)
N6	Mn2	Ca1	98.99(17)	C37	N7	Mn2	128.8(10)
N7	Mn2	Ca1	119.9(5)	C37	N7	C41	120.2(12)
N7	Mn2	N6	94.7(7)	C41	N7	Mn2	110.9(10)
N7A	Mn2	Ca1	112.5(5)	C43	N8	Mn3	122.9(5)
N7A	Mn2	N6	97.3(8)	C47	N8	Mn3	116.3(5)
O1	Mn3	Ca1	95.00(15)	C47	N8	C43	120.7(7)
O1	Mn3	O3	112.37(19)	C49	N9	Mn4	126.2(7)
O1	Mn3	O5	77.9(2)	C53	N9	Mn4	117.7(5)
O1	Mn3	O8	164.96(19)	C53	N9	C49	116.1(8)
O1	Mn3	O10	100.8(2)	C55	N10	Mn5	127.4(6)
O1	Mn3	N8	92.9(2)	C55	N10	C59	119.2(8)
O3	Mn3	Ca1	40.77(13)	C59	N10	Mn5	113.2(6)
O3	Mn3	O5	81.78(18)	Si1	N11	Mn4	115.7(4)
O3	Mn3	O8	82.66(17)	Si2	N11	Mn4	118.0(4)
O3	Mn3	N8	150.7(2)	Si2	N11	Si1	126.1(4)
O5	Mn3	Ca1	41.08(12)	Si3	N12	Mn5	116.0(4)
O5	Mn3	N8	89.7(2)	Si3	N12	Si4	122.6(4)
O8	Mn3	Ca1	96.55(13)	Si4	N12	Mn5	121.4(3)
O8	Mn3	O5	104.92(18)	N1	C1	C2	120.3(10)
O8	Mn3	N8	72.5(2)	O1S	C1S	C2S	106(2)
O10	Mn3	Ca1	133.99(14)	C2T	C1T	O1T	104.1(15)
O10	Mn3	O3	93.53(19)	C3	C2	C1	121.4(9)
O10	Mn3	O5	174.13(19)	C1S	C2S	C3S	104.9(19)
O10	Mn3	O8	77.82(19)	C1T	C2T	C3T	105.6(14)
O10	Mn3	N8	96.1(2)	C4	C3	C2	117.7(9)
N8	Mn3	Ca1	126.12(17)	C4S	C3S	C2S	104.9(17)
O2	Mn4	Ca1	84.32(16)	C4T	C3T	C2T	105.1(15)
O2	Mn4	O9	79.8(2)	C3	C4	C5	121.4(10)
O2	Mn4	N9	98.8(2)	O1S	C4S	C3S	107.7(19)
O2	Mn4	N11	119.3(2)	O1T	C4T	C3T	106.9(16)
O4	Mn4	Ca1	38.20(14)	N1	C5	C4	120.5(9)
O4	Mn4	O2	106.9(2)	N1	C5	C6	115.9(8)
O4	Mn4	O9	80.50(19)	C4	C5	C6	123.6(9)
O4	Mn4	N9	138.2(2)	O2S	C5S	C6S	106.3(13)
O4	Mn4	N11	104.2(2)	O2T	C5T	C6T	111.8(19)
O9	Mn4	Ca1	45.25(13)	O1	C6	C5	112.8(8)
O9	Mn4	N9	72.2(2)	C7S	C6S	C5S	102.3(13)
N9	Mn4	Ca1	116.0(2)	C7T	C6T	C5T	103.5(17)
N11	Mn4	Ca1	142.33(18)	N2	C7	C8	121.7(11)

N11	Mn4	O9	156.7(2)	C8S	C7S	C6S	102.1(13)
N11	Mn4	N9	90.6(3)	C6T	C7T	C8T	105.3(18)
O6	Mn5	O8	80.02(19)	C9	C8	C7	119.0(10)
O6	Mn5	O10	107.3(2)	O2S	C8S	C7S	109.6(13)
O6	Mn5	N10	92.6(2)	O2T	C8T	C7T	110(2)
O6	Mn5	N12	120.6(2)	C8	C9	C10	120.9(10)
O8	Mn5	N10	148.6(2)	C9	C10	C11	119.0(11)
O10	Mn5	O8	78.9(2)	N2	C11	C10	121.3(9)
O10	Mn5	N10	74.3(2)	N2	C11	C12	116.9(7)
O10	Mn5	N12	132.1(2)	C10	C11	C12	121.8(9)
N12	Mn5	O8	108.7(2)	O2	C12	C11	111.8(7)
N12	Mn5	N10	101.3(3)	N3	C13	C14	123.2(8)
O3	Ca1	O9	82.85(16)	C15	C14	C13	118.7(8)
O3	Ca1	N3	64.25(19)	C14	C15	C16	119.9(9)
O3	Ca1	N4	128.77(19)	C15	C16	C17	118.1(9)
O3	Ca1	N5	131.9(2)	N3	C17	C16	122.7(7)
O4	Ca1	O3	143.00(18)	N3	C17	C18	117.4(7)
O4	Ca1	O5	117.34(18)	C16	C17	C18	120.0(8)
O4	Ca1	O7	140.25(18)	O3	C18	C17	112.1(6)
O4	Ca1	O9	68.59(17)	N4	C19	C20	123.1(9)
O4	Ca1	N3	87.9(2)	C21	C20	C19	117.5(9)
O4	Ca1	N4	63.9(2)	C22	C21	C20	119.8(8)
O4	Ca1	N5	80.4(2)	C21	C22	C23	119.9(9)
O5	Ca1	O3	73.14(16)	N4	C23	C22	121.0(8)
O5	Ca1	O9	73.00(16)	N4	C23	C24	117.6(7)
O5	Ca1	N3	132.4(2)	C22	C23	C24	121.2(8)
O5	Ca1	N4	145.45(19)	O4	C24	C23	113.4(7)
O5	Ca1	N5	65.49(19)	N5	C25	C26	124.9(8)
O7	Ca1	O3	71.65(17)	C25	C26	C27	118.2(9)
O7	Ca1	O5	86.40(17)	C28	C27	C26	118.4(8)
O7	Ca1	O9	151.07(17)	C27	C28	C29	121.1(8)
O7	Ca1	N3	98.98(19)	N5	C29	C28	120.9(8)
O7	Ca1	N4	78.5(2)	N5	C29	C30	116.3(7)
O7	Ca1	N5	82.03(19)	C28	C29	C30	122.8(8)
O9	Ca1	N3	81.35(18)	O5	C30	C29	113.3(6)
O9	Ca1	N4	129.6(2)	N6	C31	C32	123.9(8)
O9	Ca1	N5	106.45(19)	C31	C32	C33	116.8(8)
N3	Ca1	N4	81.0(2)	C32	C33	C34	121.6(9)
N3	Ca1	N5	162.1(2)	C33	C34	C35	117.3(8)
N5	Ca1	N4	81.6(2)	N6	C35	C34	121.5(7)
N11	Si1	C61	110.6(4)	N6	C35	C36	118.1(7)
N11	Si1	C62	114.7(4)	C34	C35	C36	120.5(8)

N11	Si1	C63	112.1(4)	O6	C36	C35	112.1(7)
C61	Si1	C62	108.1(4)	N7	C37	C38	121.2(13)
C61	Si1	C63	106.3(5)	C39	C38	C37	119.2(14)
C62	Si1	C63	104.5(5)	C38	C39	C40	119.4(14)
N11	Si2	C64	109.9(4)	C41	C40	C39	118.6(13)
N11	Si2	C65	111.9(4)	N7	C41	C40	121.2(12)
N11	Si2	C66	115.7(4)	N7	C41	C42	116.6(13)
C65	Si2	C64	108.4(5)	C40	C41	C42	122.2(12)
C65	Si2	C66	106.2(5)	O7	C42	C41	118.7(13)
C66	Si2	C64	104.2(5)	N8	C43	C44	121.3(8)
N12	Si3	C67	113.7(4)	C43	C44	C45	119.1(8)
N12	Si3	C68	113.4(4)	C46	C45	C44	119.1(8)
N12	Si3	C69	111.8(4)	C45	C46	C47	119.7(8)
C67	Si3	C68	106.1(4)	N8	C47	C46	120.1(7)
C69	Si3	C67	105.9(4)	N8	C47	C48	118.2(7)
C69	Si3	C68	105.2(5)	C46	C47	C48	121.7(7)
N12	Si4	C70	111.8(4)	O8	C48	C47	111.9(6)
N12	Si4	C71	113.4(4)	N9	C49	C50	123.6(10)
N12	Si4	C72	114.8(4)	C51	C50	C49	119.0(10)
C71	Si4	C70	107.0(4)	C52	C51	C50	117.4(9)
C71	Si4	C72	105.0(5)	C53	C52	C51	120.6(9)
C72	Si4	C70	104.0(4)	N9	C53	C52	123.3(8)
Mn3	O1	Mn1	103.3(2)	N9	C53	C54	113.9(7)
C6	O1	Mn1	121.5(5)	C52	C53	C54	122.8(9)
C6	O1	Mn3	134.0(5)	O9	C54	C53	114.4(7)
C4S	O1S	C1S	109(2)	N10	C55	C56	122.4(10)
C4T	O1T	C1T	104.0(15)	C57	C56	C55	119.1(11)
Mn4	O2	Mn1	101.9(2)	C58	C57	C56	119.0(10)
C12	O2	Mn1	118.5(5)	C57	C58	C59	119.2(10)
C12	O2	Mn4	133.9(5)	N10	C59	C58	121.1(9)
C5S	O2S	C8S	109.7(13)	N10	C59	C60	117.3(8)
C5T	O2T	C8T	106(2)	C58	C59	C60	121.6(9)
Mn2	O3	Mn3	97.53(19)	O10	C60	C59	113.8(7)
Mn2	O3	Ca1	100.52(18)	N7A	C37A	C38A	124.1(15)
Mn3	O3	Ca1	103.71(19)	C39A	C38A	C37A	116.1(15)
C18	O3	Mn2	115.2(4)	C37A	N7A	Mn2	123.9(12)
C18	O3	Mn3	115.0(4)	C37A	N7A	C41A	118.7(14)
C18	O3	Ca1	121.3(4)	C41A	N7A	Mn2	114.9(11)
Mn4	O4	Ca1	108.9(2)	O7	C42A	C41A	108.0(14)
C24	O4	Mn4	122.6(5)	C39A	C40A	C41A	118.5(14)
C24	O4	Ca1	128.4(4)	C38A	C39A	C40A	121.3(15)
Mn1	O5	Mn3	97.62(19)	N7A	C41A	C42A	117.9(14)

Mn1	O5	Ca1	99.56(19)	N7A	C41A	C40A	121.0(14)
Mn3	O5	Ca1	101.26(19)	C40A	C41A	C42A	121.0(13)
C30	O5	Mn1	122.6(4)				

Experimental

A single crystal of $C_{80}H_{112}CaMn_5N_{12}O_{12}Si_4$ was selected and mounted on a diffractometer. The crystal was kept at 100.03 K during data collection. The structure was solved with the SHELXS structure solution program and refined with the SHELXL refinement package using least squares minimization using OLEX2 [1] as a GUI.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

Crystal structure determination of 3·2THF

Crystal Data for $C_{80}H_{112}CaMn_5N_{12}O_{12}Si_4$ (M =1860.95 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 15.598(4) Å, b = 16.828(4) Å, c = 43.150(11) Å, β = 91.079(5)°, V = 11324(5) Å^3, Z = 4, T = 100.03 K, μ(MoKα) = 0.680 mm^{-1}, *Dcalc* = 1.092 g/cm^3, 50837 reflections measured (3.07° ≤ 2Θ ≤ 41.872°), 11966 unique (R_{int} = 0.1078, R_{sigma} = 0.0938) which were used in all calculations. The final R_1 was 0.0679 (I > 2σ(I)) and wR_2 was 0.1896 (all data).

Refinement model description

Number of restraints - 730, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All C(H,H) groups

At 1.5 times of:

All C(H,H,H) groups

2. Restrained distances

O1S-C1S = O1T-C1T = O1T-C4T = O1S-C4S

1.45 with sigma of 0.02

C2S-C1S = C2T-C1T = C3S-C2S = C3T-C2T = C4T-C3T = C4S-C3S

1.54 with sigma of 0.02

O2T-C8T = O2S-C8S = O2T-C5T = O2S-C5S

1.45 with sigma of 0.02

C8S-C7S = C8T-C7T = C7T-C6T = C7S-C6S = C6T-C5T = C6S-C5S

1.54 with sigma of 0.02

N7-C37 = N7A-C37A = N7A-C41A = N7-C41

1.34 with sigma of 0.02

C41A-C40A = C41-C40 = C40A-C39A = C40-C39 = C39A-C38A = C39-C38 = C38A-C37A = C38-C37

1.39 with sigma of 0.02

C42A-C41A = C42-C41

1.5 with sigma of 0.02

O7-C42A = O7-C42

1.45 with sigma of 0.02

Mn2-N7 = Mn2-N7A
2.27 with sigma of 0.02
C1T-C4T
2.29 with sigma of 0.04
C4S-C1S
2.29 with sigma of 0.04
O1S-C2S
2.44 with sigma of 0.04
O1S-C3S
2.44 with sigma of 0.04
O1T-C2T
2.44 with sigma of 0.04
O1T-C3T
2.44 with sigma of 0.04
C1T-C3T
2.52 with sigma of 0.04
C2T-C4T
2.52 with sigma of 0.04
C4S-C2S
2.52 with sigma of 0.04
C3S-C1S
2.52 with sigma of 0.04
O2S-C7S
2.44 with sigma of 0.04
O2S-C6S
2.44 with sigma of 0.04
O2T-C6T
2.44 with sigma of 0.04
O2T-C7T
2.44 with sigma of 0.04
C8T-C5T
2.29 with sigma of 0.04
C8S-C5S
2.29 with sigma of 0.04
C8T-C6T
2.52 with sigma of 0.04
C7T-C5T
2.52 with sigma of 0.04
C5S-C7S
2.52 with sigma of 0.04
C6S-C8S
2.52 with sigma of 0.04
C41A-C37A
2.32 with sigma of 0.04
C41-C37
2.32 with sigma of 0.04

N7A-C40A
2.36 with sigma of 0.04
N7A-C38A
2.36 with sigma of 0.04
N7-C40
2.36 with sigma of 0.04
N7-C38
2.36 with sigma of 0.04
C41A-C39A
2.41 with sigma of 0.04
C40A-C38A
2.41 with sigma of 0.04
C39A-C37A
2.41 with sigma of 0.04
C37-C39
2.41 with sigma of 0.04
C38-C40
2.41 with sigma of 0.04
C39-C41
2.41 with sigma of 0.04
C42A-C40A
2.5 with sigma of 0.04
C42-C40
2.5 with sigma of 0.04
N7A-C42A
2.46 with sigma of 0.04
C42-N7
2.46 with sigma of 0.04
3. Rigid bond restraints
O1S, O1T, C1S, C1T, C2S, C2T, C3S, C3T, C4S, C4T
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
O2S, O2T, C5S, C5T, C6S, C6T, C7S, C7T, C8S, C8T
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
N7, C37, C38, C39, C40, C41, C42, C37A, C38A, N7A, C42A, C40A, C39A, C41A, O7
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
4. Uiso/Uaniso restraints and constraints
O1S ≈ O1T ≈ C1S ≈ C1T ≈ C2S ≈ C2T ≈ C3S ≈ C3T ≈
C4S ≈ C4T: within 2A with sigma of 0.04 and sigma for terminal atoms of 0.08
O2S ≈ O2T ≈ C5S ≈ C5T ≈ C6S ≈ C6T ≈ C7S ≈ C7T ≈
C8S ≈ C8T: within 2A with sigma of 0.04 and sigma for terminal atoms of 0.08
N7 ≈ C37 ≈ C38 ≈ C39 ≈ C40 ≈ C41 ≈ C42 ≈ C37A ≈
C38A ≈ N7A ≈ C42A ≈ C40A ≈ C39A ≈ C41A ≈ O7: within 2A
with sigma of 0.01 and sigma for terminal atoms of 0.02
Uanis(N7) ≈ Ueq, Uanis(C37) ≈ Ueq, Uanis(C38) ≈ Ueq, Uanis(C39)
≈ Ueq, Uanis(C40) ≈ Ueq, Uanis(C41) ≈ Ueq, Uanis(C42) ≈ Ueq,
Uanis(C37A) ≈ Ueq, Uanis(C38A) ≈ Ueq, Uanis(N7A) ≈ Ueq, Uanis(C42A)

≈ Ueq, Uanis(C40A) ≈ Ueq, Uanis(C39A) ≈ Ueq, Uanis(C41A) ≈ Ueq:
with sigma of 0.01 and sigma for terminal atoms of 0.02
5. Others
Sof(O1T)=Sof(C1T)=Sof(H1TA)=Sof(H1TB)=Sof(C2T)=Sof(H2TA)=Sof(H2TB)=Sof(C3T)=
Sof(H3TA)=Sof(H3TB)=Sof(C4T)=Sof(H4TA)=Sof(H4TB)=1-FVAR(1)
Sof(O1S)=Sof(C1S)=Sof(H1SA)=Sof(H1SB)=Sof(C2S)=Sof(H2SA)=Sof(H2SB)=Sof(C3S)=
Sof(H3SA)=Sof(H3SB)=Sof(C4S)=Sof(H4SA)=Sof(H4SB)=FVAR(1)
Sof(O2T)=Sof(C5T)=Sof(H5TA)=Sof(H5TB)=Sof(C6T)=Sof(H6TA)=Sof(H6TB)=Sof(C7T)=
Sof(H7TA)=Sof(H7TB)=Sof(C8T)=Sof(H8TA)=Sof(H8TB)=1-FVAR(2)
Sof(O2S)=Sof(C5S)=Sof(H5SA)=Sof(H5SB)=Sof(C6S)=Sof(H6SA)=Sof(H6SB)=Sof(C7S)=
Sof(H7SA)=Sof(H7SB)=Sof(C8S)=Sof(H8SA)=Sof(H8SB)=FVAR(2)
Sof(C37A)=Sof(H37A)=Sof(C38A)=Sof(H38A)=Sof(N7A)=Sof(C42A)=Sof(H42C)=
Sof(H42D)=Sof(C40A)=Sof(H40A)=Sof(C39A)=Sof(H39A)=Sof(C41A)=1-FVAR(3)
Sof(N7)=Sof(C37)=Sof(H37)=Sof(C38)=Sof(H38)=Sof(C39)=Sof(H39)=Sof(C40)=
Sof(H40)=Sof(C41)=Sof(C42)=Sof(H42A)=Sof(H42B)=FVAR(3)
6.a Secondary CH2 refined with riding coordinates:
C1S(H1SA,H1SB), C1T(H1TA,H1TB), C2S(H2SA,H2SB), C2T(H2TA,H2TB), C3S(H3SA,
H3SB), C3T(H3TA,H3TB), C4S(H4SA,H4SB), C4T(H4TA,H4TB), C5S(H5SA,H5SB),
C5T(H5TA,H5TB), C6(H6A,H6B), C6S(H6SA,H6SB), C6T(H6TA,H6TB),
C7S(H7SA,H7SB),
C7T(H7TA,H7TB), C8S(H8SA,H8SB), C8T(H8TA,H8TB), C12(H12A,H12B),
C18(H18A,H18B),
C24(H24A,H24B), C30(H30A,H30B), C36(H36A,H36B), C42(H42A,H42B), C48(H48A,
H48B), C54(H54A,H54B), C60(H60A,H60B), C42A(H42C,H42D)
6.b Aromatic/amide H refined with riding coordinates:
C1(H1), C2(H2), C3(H3), C4(H4), C7(H7), C8(H8), C9(H9), C10(H10), C13(H13),
C14(H14), C15(H15), C16(H16), C19(H19), C20(H20), C21(H21), C22(H22), C25(H25),
C26(H26), C27(H27), C28(H28), C31(H31), C32(H32), C33(H33), C34(H34),
C37(H37), C38(H38), C39(H39), C40(H40), C43(H43), C44(H44), C45(H45), C46(H46),
C49(H49), C50(H50), C51(H51), C52(H52), C55(H55), C56(H56), C57(H57),
C58(H58), C37A(H37A), C38A(H38A), C40A(H40A), C39A(H39A)
6.c Idealised Me refined as rotating group:
C61(H61A,H61B,H61C), C62(H62A,H62B,H62C), C63(H63A,H63B,H63C),
C64(H64A,H64B,
H64C), C65(H65A,H65B,H65C), C66(H66A,H66B,H66C), C67(H67A,H67B,H67C),
C68(H68A,
H68B,H68C), C69(H69A,H69B,H69C), C70(H70A,H70B,H70C), C71(H71A,H71B,H71C),
C72(H72A,H72B,H72C)
This report has been created with Olex2, compiled on 2018.05.29 svn.r3508 for OlexSys.
Please let us know if there are any errors or if you would like to have additional features.

4·5.27 THF

Table S11 Crystal data and structure refinement for 4·5.27THF.

Empirical formula	$C_{93.08}H_{138.16}Ca_2Mn_4N_{12}O_{15.27}Si_4$
Formula weight	2081.87
Temperature/K	99.97
Crystal system	triclinic
Space group	P-1
a/Å	13.071(4)
b/Å	14.016(5)
c/Å	15.223(5)
α/°	79.579(5)
β/°	73.067(5)
γ/°	83.215(5)
Volume/Å^3	2617.7(15)
Z	1
ρ_{calc}g/cm^3	1.321
μ/mm^{-1}	0.680
F(000)	1099.0
Crystal size/mm^3	0.21 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.83 to 55.812
Index ranges	-16 ≤ h ≤ 17, -18 ≤ k ≤ 18, -20 ≤ l ≤ 19
Reflections collected	44632
Independent reflections	12166 [R_{int} = 0.0549, R_{sigma} = 0.0732]
Data/restraints/parameters	12166/698/760
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0555, wR_2 = 0.1341
Final R indexes [all data]	R_1 = 0.1067, wR_2 = 0.1589
Largest diff. peak/hole / e Å^{-3}	1.16/-0.56

Table S12 Bond Lengths for 4·5.27 THF.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	Mn2	3.2108(11)	O3S	C12S	1.484(11)
Mn1	Ca1	3.4440(11)	C9S	C10S	1.472(13)
Mn1	Ca1[1]	3.4790(12)	C10S	C11S	1.533(13)
Mn1	O1	2.159(2)	C11S	C12S	1.438(13)
Mn1	O2	2.119(2)	O3T	C9T	1.489(14)
Mn1	O4	2.144(2)	O3T	C12T	1.519(14)
Mn1	O5	2.220(2)	C9T	C10T	1.576(19)
Mn1	N1	2.317(3)	C10T	C11T	1.544(19)
Mn1	N2	2.288(3)	C11T	C12T	1.566(19)
Mn2	O1	2.081(2)	O4	C24	1.395(4)
Mn2	O3	2.088(2)	O5	C30	1.403(4)
Mn2	O5	2.210(2)	N1	C1	1.332(5)
Mn2	N5	2.344(3)	N1	C5	1.340(12)
Mn2	N6	2.119(3)	N1	C5A	1.334(13)
Ca1	O2	2.299(2)	N2	C7	1.346(4)
Ca1	O3[1]	2.334(3)	N2	C11	1.327(4)
Ca1	O4[1]	2.384(2)	N3	C13	1.335(5)
Ca1	O4	2.412(2)	N3	C17	1.323(5)
Ca1	O5[1]	2.402(2)	N4	C19	1.350(5)
Ca1	N3[1]	2.711(3)	N4	C23	1.339(5)
Ca1	N4	2.550(3)	N5	C25	1.352(4)
Si1	N6	1.686(3)	N5	C29	1.326(5)
Si1	C34	1.886(4)	C1	C2	1.396(13)
Si1	C35	1.888(4)	C1	C2A	1.387(14)
Si1	C36	1.869(4)	C2	C3	1.373(13)
Si2	N6	1.695(3)	C2A	C3A	1.377(14)
Si2	C31	1.878(4)	C3	C4	1.363(12)
Si2	C32	1.872(4)	C3A	C4A	1.367(13)
Si2	C33	1.876(5)	C4	C5	1.387(12)
O1	C6	1.36(2)	C4A	C5A	1.374(13)
O1	C6A	1.42(3)	C5	C6	1.506(13)
O1S	C1S	1.439(6)	C5A	C6A	1.513(15)
O1S	C4S	1.456(8)	C7	C8	1.377(5)
O1S	C4T	1.471(12)	C8	C9	1.391(6)
C1S	C2S	1.495(7)	C9	C10	1.372(6)
C2S	C3S	1.511(7)	C10	C11	1.397(5)
C3S	C4S	1.465(10)	C11	C12	1.525(5)
C3S	C4T	1.639(15)	C13	C14	1.384(6)
O2	C12	1.386(4)	C14	C15	1.375(6)
O2S	C5S	1.383(9)	C15	C16	1.364(6)

O2S	C8S	1.461(9)	C16	C17	1.395(5)
C5S	C6S	1.513(12)	C17	C18	1.502(5)
C6S	C7S	1.452(11)	C19	C20	1.377(6)
C7S	C8S	1.547(12)	C20	C21	1.373(6)
O2T	C5T	1.509(13)	C21	C22	1.377(6)
O2T	C6T	1.501(13)	C22	C23	1.386(5)
C5T	C8T	1.589(19)	C23	C24	1.514(5)
C5T	C11T	1.76(4)	C25	C26	1.369(5)
C6T	C7T	1.532(19)	C26	C27	1.377(6)
C7T	C8T	1.527(19)	C27	C28	1.371(5)
O3	C18	1.391(4)	C28	C29	1.397(5)
O3S	C9S	1.474(11)	C29	C30	1.510(5)

[1]1-X,1-Y,1-Z

Table S13 Bond Angles for 4·5.27 THF.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Mn2	Mn1	Ca1[1]	63.38(2)	O2T	C5T	C11T	103.5(19)
Mn2	Mn1	Ca1	129.51(2)	C8T	C5T	C11T	144(2)
Ca1	Mn1	Ca1[1]	66.13(3)	O2T	C6T	C7T	105.8(16)
O1	Mn1	Mn2	39.87(6)	C8T	C7T	C6T	111.4(18)
O1	Mn1	Ca1[1]	96.00(7)	C7T	C8T	C5T	100.6(17)
O1	Mn1	Ca1	151.57(7)	Mn2	O3	Ca1[1]	105.46(11)
O1	Mn1	O5	82.89(9)	C18	O3	Mn2	121.8(2)
O1	Mn1	N1	73.14(10)	C18	O3	Ca1[1]	124.3(2)
O1	Mn1	N2	93.51(10)	C9S	O3S	C12S	112.0(9)
O2	Mn1	Mn2	140.95(7)	C10S	C9S	O3S	101.3(8)
O2	Mn1	Ca1[1]	92.77(7)	C9S	C10S	C11S	109.1(9)
O2	Mn1	Ca1	40.70(6)	C12S	C11S	C10S	107.6(9)
O2	Mn1	O1	167.72(9)	C11S	C12S	O3S	103.6(9)
O2	Mn1	O4	84.33(9)	C9T	O3T	C12T	101.2(19)
O2	Mn1	O5	97.82(9)	O3T	C9T	C10T	101.5(17)
O2	Mn1	N1	106.95(10)	C11T	C10T	C9T	111.1(17)
O2	Mn1	N2	74.23(10)	C10T	C11T	C5T	114(3)
O4	Mn1	Mn2	94.97(7)	C10T	C11T	C12T	95.2(17)
O4	Mn1	Ca1	43.90(6)	C12T	C11T	C5T	116(3)
O4	Mn1	Ca1[1]	42.41(6)	O3T	C12T	C11T	104.5(19)
O4	Mn1	O1	107.94(9)	Mn1	O4	Ca1[1]	100.25(9)
O4	Mn1	O5	85.57(8)	Mn1	O4	Ca1	98.03(9)
O4	Mn1	N1	95.74(9)	Ca1[1]	O4	Ca1	103.91(9)
O4	Mn1	N2	158.54(10)	C24	O4	Mn1	119.27(19)
O5	Mn1	Mn2	43.43(6)	C24	O4	Ca1	118.1(2)
O5	Mn1	Ca1[1]	43.20(6)	C24	O4	Ca1[1]	114.31(19)
O5	Mn1	Ca1	96.20(6)	Mn1	O5	Ca1[1]	97.57(9)
O5	Mn1	N1	155.22(10)	Mn2	O5	Mn1	92.90(9)
O5	Mn1	N2	97.82(9)	Mn2	O5	Ca1[1]	99.47(9)
N1	Mn1	Mn2	111.95(8)	C30	O5	Mn1	113.21(19)
N1	Mn1	Ca1[1]	132.23(7)	C30	O5	Mn2	118.53(19)
N1	Mn1	Ca1	101.86(8)	C30	O5	Ca1[1]	128.07(18)
N2	Mn1	Mn2	102.06(8)	C1	N1	Mn1	127.3(2)
N2	Mn1	Ca1[1]	137.68(7)	C1	N1	C5	119.9(6)
N2	Mn1	Ca1	114.67(8)	C1	N1	C5A	116.6(7)
N2	Mn1	N1	89.96(10)	C5	N1	Mn1	111.2(6)
O1	Mn2	O3	99.06(10)	C5A	N1	Mn1	116.0(7)
O1	Mn2	O5	84.93(9)	C7	N2	Mn1	125.7(2)
O1	Mn2	N5	93.65(10)	C11	N2	Mn1	115.1(2)
O1	Mn2	N6	123.10(11)	C11	N2	C7	119.1(3)

O3	Mn2	O5	81.74(9)	C13	N3	Ca1[1]	128.7(3)
O3	Mn2	N5	149.42(11)	C17	N3	Ca1[1]	113.5(2)
O3	Mn2	N6	104.37(11)	C17	N3	C13	117.3(3)
O5	Mn2	N5	71.77(9)	C19	N4	Ca1	125.5(3)
N6	Mn2	O5	148.84(11)	C23	N4	Ca1	116.4(2)
N6	Mn2	N5	91.42(11)	C23	N4	C19	117.4(3)
O2	Ca1	O3[1]	114.65(9)	C25	N5	Mn2	125.5(3)
O2	Ca1	O4[1]	93.49(9)	C29	N5	Mn2	116.5(2)
O2	Ca1	O4	74.79(8)	C29	N5	C25	117.9(3)
O2	Ca1	O5[1]	167.53(9)	Si1	N6	Mn2	115.40(17)
O2	Ca1	N3[1]	77.63(9)	Si1	N6	Si2	127.89(19)
O2	Ca1	N4	100.53(9)	Si2	N6	Mn2	116.61(16)
O3[1]	Ca1	O4[1]	87.33(9)	N1	C1	C2	119.1(7)
O3[1]	Ca1	O4	161.65(8)	N1	C1	C2A	127.0(8)
O3[1]	Ca1	O5[1]	72.88(8)	C3	C2	C1	121.6(11)
O3[1]	Ca1	N3[1]	64.06(9)	C3A	C2A	C1	114.6(12)
O3[1]	Ca1	N4	123.88(10)	C4	C3	C2	118.3(10)
O4[1]	Ca1	O4	76.10(9)	C4A	C3A	C2A	119.5(11)
O4[1]	Ca1	O5[1]	76.54(8)	C3	C4	C5	118.7(10)
O4	Ca1	N3[1]	134.28(9)	C3A	C4A	C5A	121.6(11)
O4[1]	Ca1	N3[1]	141.64(10)	N1	C5	C4	122.5(10)
O4[1]	Ca1	N4	134.18(9)	N1	C5	C6	117.1(11)
O4	Ca1	N4	66.22(9)	C4	C5	C6	120.4(12)
O5[1]	Ca1	O4	95.29(8)	N1	C5A	C4A	120.6(12)
O5[1]	Ca1	N3[1]	114.83(9)	N1	C5A	C6A	116.8(14)
O5[1]	Ca1	N4	81.80(9)	C4A	C5A	C6A	122.5(14)
N4	Ca1	N3[1]	84.15(10)	O1	C6	C5	113.8(13)
N6	Si1	C34	114.03(18)	O1	C6A	C5A	112.2(17)
N6	Si1	C35	114.52(17)	N2	C7	C8	122.5(3)
N6	Si1	C36	110.25(17)	C7	C8	C9	118.4(4)
C34	Si1	C35	105.6(2)	C10	C9	C8	118.9(4)
C36	Si1	C34	105.22(19)	C9	C10	C11	119.6(4)
C36	Si1	C35	106.5(2)	N2	C11	C10	121.4(3)
N6	Si2	C31	110.71(19)	N2	C11	C12	116.6(3)
N6	Si2	C32	112.45(17)	C10	C11	C12	122.0(3)
N6	Si2	C33	115.4(2)	O2	C12	C11	113.0(3)
C32	Si2	C31	107.3(2)	N3	C13	C14	124.1(4)
C32	Si2	C33	105.2(2)	C15	C14	C13	118.0(4)
C33	Si2	C31	105.1(3)	C16	C15	C14	118.6(4)
Mn2	O1	Mn1	98.43(9)	C15	C16	C17	119.9(4)
C6	O1	Mn1	115.7(7)	N3	C17	C16	122.1(4)
C6	O1	Mn2	127.7(7)	N3	C17	C18	117.9(3)

C6A	O1	Mn1	119.9(8)	C16	C17	C18	120.0(3)
C6A	O1	Mn2	135.2(9)	O3	C18	C17	113.7(3)
C1S	O1S	C4S	108.1(5)	N4	C19	C20	123.6(4)
C1S	O1S	C4T	100.6(8)	C21	C20	C19	118.4(4)
O1S	C1S	C2S	105.0(4)	C20	C21	C22	118.9(4)
C1S	C2S	C3S	103.1(5)	C21	C22	C23	119.7(4)
C2S	C3S	C4T	103.4(6)	N4	C23	C22	122.0(3)
C4S	C3S	C2S	100.0(5)	N4	C23	C24	117.3(3)
O1S	C4S	C3S	105.1(6)	C22	C23	C24	120.7(4)
O1S	C4T	C3S	96.3(8)	O4	C24	Ca1[1]	42.44(14)
Mn1	O2	Ca1	102.36(10)	O4	C24	C23	113.6(3)
C12	O2	Mn1	120.5(2)	C23	C24	Ca1[1]	149.1(2)
C12	O2	Ca1	137.1(2)	N5	C25	C26	123.1(4)
C5S	O2S	C8S	113.1(8)	C25	C26	C27	118.6(3)
O2S	C5S	C6S	105.9(8)	C28	C27	C26	119.3(4)
C7S	C6S	C5S	108.2(8)	C27	C28	C29	118.9(4)
C6S	C7S	C8S	104.7(8)	N5	C29	C28	122.2(3)
O2S	C8S	C7S	104.0(8)	N5	C29	C30	116.3(3)
C6T	O2T	C5T	108.4(16)	C28	C29	C30	121.5(3)
O2T	C5T	C8T	108.2(17)	O5	C30	C29	112.7(3)

[1]1-X,1-Y,1-Z

Experimental

A single crystal of $C_{93.08}H_{138.16}Ca_2Mn_4N_{12}O_{15.27}Si_4$ was selected and mounted on a diffractometer. The crystal was kept at 99.97 K during data collection. The structure was solved with the SHELXS structure solution program and refined with SHELXL using least squares minimization using Olex2 [1] as a GUI.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

Crystal structure determination of 4·5.27 THF

Crystal Data for $C_{93.08}H_{138.16}Ca_2Mn_4N_{12}O_{15.27}Si_4$ (M =2081.87 g/mol): triclinic, space group P-1 (no. 2), a = 13.071(4) Å, b = 14.016(5) Å, c = 15.223(5) Å, α = 79.579(5)°, β = 73.067(5)°, γ = 83.215(5)°, V = 2617.7(15) Å^3, Z = 1, T = 99.97 K, μ(MoKα) = 0.680 mm^{-1}, *Dcalc* = 1.321 g/cm^3, 44632 reflections measured (2.83° ≤ 2Θ ≤ 55.812°), 12166 unique (R_{int} = 0.0549, R_{sigma} = 0.0732) which were used in all calculations. The final R_1 was 0.0555 (I > 2σ(I)) and wR_2 was 0.1589 (all data).

Refinement model description

Number of restraints - 698, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All C(H,H) groups, All C(H,H,H,H) groups

At 1.5 times of:
All C(H,H,H) groups
2. Restrained distances
N1-C5A = N1-C5
1.34 with sigma of 0.02
C2A-C1 = C2-C1 = C3A-C2A = C3-C2 = C4A-C3A = C4-C3 = C5A-C4A = C5-C4
1.39 with sigma of 0.02
C6A-C5A = C6-C5
1.5 with sigma of 0.02
C8T-C5T = C8T-C7T = C7T-C6T = C6S-C5S = C7S-C6S = C8S-C7S = C4T-C3S = C4S-C3S = C3S-C2S = C2S-C1S = C9S-C10S = C11S-C10S = C12S-C11S = C9T-C10T = C11T-C10T = C12T-C11T
1.54 with sigma of 0.02
O2T-C6T = O2T-C5T = O2S-C8S = O2S-C5S = O3T-C9T = O3T-C12T = O3S-C12S = O3S-C9S = O1S-C4T = O1S-C4S = O1S-C1S
1.54 with sigma of 0.02
O2T-C5T = O2T-C6T = O2S-C5S = O2S-C8S = O1S-C4T = O1S-C4S = O1S-C1S = O3T-C9T = O3T-C12T = O3S-C12S = O3S-C9S
1.45 with sigma of 0.02
N1-C4A
2.34 with sigma of 0.04
N1-C4
2.34 with sigma of 0.04
N1-C2A
2.34 with sigma of 0.04
N1-C2
2.34 with sigma of 0.04
C5A-C1
2.32 with sigma of 0.04
C5-C1
2.32 with sigma of 0.04
C5A-C3A
2.41 with sigma of 0.04
C4A-C2A
2.41 with sigma of 0.04
C3A-C1
2.41 with sigma of 0.04
C5-C3
2.41 with sigma of 0.04
C4-C2
2.41 with sigma of 0.04
C3-C1
2.41 with sigma of 0.04
C4A-C6A
2.5 with sigma of 0.04
C4-C6

2.5 with sigma of 0.04
N1-C6A
2.46 with sigma of 0.04
N1-C6
2.46 with sigma of 0.04
O2S-C7S
2.44 with sigma of 0.04
O2S-C6S
2.44 with sigma of 0.04
O1S-C3S
2.44 with sigma of 0.04
O1S-C2S
2.44 with sigma of 0.04
O3T-C11T
2.44 with sigma of 0.04
O3T-C10T
2.44 with sigma of 0.04
O3S-C11S
2.44 with sigma of 0.04
O3S-C10S
2.44 with sigma of 0.04
C8S-C5S
2.29 with sigma of 0.04
C5T-C6T
2.29 with sigma of 0.04
C12T-C9T
2.29 with sigma of 0.04
C12S-C9S
2.29 with sigma of 0.04
C1S-C4T
2.29 with sigma of 0.04
C1S-C4S
2.29 with sigma of 0.04
C6T-C8T
2.52 with sigma of 0.04
C7T-C5T
2.52 with sigma of 0.04
C5S-C7S
2.52 with sigma of 0.04
C6S-C8S
2.52 with sigma of 0.04
C9T-C11T
2.52 with sigma of 0.04
C10T-C12T
2.52 with sigma of 0.04
C12S-C10S

2.52 with sigma of 0.04
C11S-C9S
2.52 with sigma of 0.04
C4T-C2S
2.52 with sigma of 0.04
C4S-C2S
2.52 with sigma of 0.04
C3S-C1S
2.52 with sigma of 0.04
3. Restrained planarity
N1, C1, C2A, C3A, C4A, C5A, C6A
with sigma of 0.1
N1, C1, C2, C3, C4, C5, C6
with sigma of 0.1
4. Rigid bond restraints
N1, C1, C2, C2A, C3, C3A, C4, C4A, C5, C5A, C6, C6A
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
O1S, C1S, C2S, C3S, C4S, C4T, O2S, C5S, C6S, C7S, C8S, O2T, C5T, C6T, C7T,
C8T, O3S, C9S, C10S, C11S, C12S, O3T, C9T, C10T, C11T, C12T
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
5. Uiso/Uaniso restraints and constraints
N1 ≈ C1 ≈ C2 ≈ C2A ≈ C3 ≈ C3A ≈ C4 ≈ C4A ≈ C5
≈ C5A ≈ C6 ≈ C6A: within 2A with sigma of 0.04 and sigma for
terminal atoms of 0.08
O1S ≈ C1S ≈ C2S ≈ C3S ≈ C4S ≈ C4T ≈ O2S ≈ C5S ≈
C6S ≈ C7S ≈ C8S ≈ O2T ≈ C5T ≈ C6T ≈ C7T ≈ C8T ≈
O3S ≈ C9S ≈ C10S ≈ C11S ≈ C12S ≈ O3T ≈ C9T ≈ C10T
≈ C11T ≈ C12T: within 2A with sigma of 0.04 and sigma for terminal
atoms of 0.08
6. Others
Sof(H3SC)=Sof(H3SD)=Sof(C4T)=Sof(H4TA)=Sof(H4TB)=1-FVAR(1)
Sof(H3SA)=Sof(H3SB)=Sof(C4S)=Sof(H4SA)=Sof(H4SB)=FVAR(1)
Sof(O2S)=Sof(C5S)=Sof(H5SA)=Sof(H5SB)=Sof(C6S)=Sof(H6SA)=Sof(H6SB)=Sof(C7S)=
Sof(H7SA)=Sof(H7SB)=Sof(C8S)=Sof(H8SA)=Sof(H8SB)=FVAR(2)
Sof(O2T)=Sof(C5T)=Sof(H5TA)=Sof(H5TB)=Sof(C6T)=Sof(H6TA)=Sof(H6TB)=Sof(C7T)=
Sof(H7TA)=Sof(H7TB)=Sof(C8T)=Sof(H8TA)=Sof(H8TB)=FVAR(3)
Sof(O3S)=Sof(C9S)=Sof(H9SA)=Sof(H9SB)=Sof(C10S)=Sof(H10A)=Sof(H10B)=Sof(C11S)=
Sof(H11A)=Sof(H11B)=Sof(C12S)=Sof(H12C)=Sof(H12D)=FVAR(4)

Sof(O3T)=Sof(C9T)=Sof(H9TA)=Sof(H9TB)=Sof(C10T)=Sof(H10C)=Sof(H10D)=Sof(C11T)
=
Sof(H11C)=Sof(H11D)=Sof(C12T)=Sof(H12E)=Sof(H12F)=FVAR(5)
Sof(H1B)=Sof(C2A)=Sof(H2A)=Sof(C3A)=Sof(H3A)=Sof(C4A)=Sof(H4A)=Sof(C5A)=
Sof(C6A)=Sof(H6AA)=Sof(H6AB)=1-FVAR(6)
Sof(H1A)=Sof(C2)=Sof(H2)=Sof(C3)=Sof(H3)=Sof(C4)=Sof(H4)=Sof(C5)=Sof(C6)=
Sof(H6B)=Sof(H6A)=FVAR(6)

7.a Secondary CH2 refined with riding coordinates:
C1S(H1SA,H1SB), C2S(H2SA,H2SB), C3S(H3SA,H3SB), C3S(H3SC,H3SD), C4S(H4SA,
H4SB), C4T(H4TA,H4TB), C5S(H5SA,H5SB), C6S(H6SA,H6SB), C7S(H7SA,H7SB),
C8S(H8SA,H8SB), C5T(H5TA,H5TB), C6T(H6TA,H6TB), C7T(H7TA,H7TB),
C8T(H8TA,H8TB),
C9S(H9SA,H9SB), C10S(H10A,H10B), C11S(H11A,H11B), C12S(H12C,H12D), C9T(H9TA,
H9TB), C10T(H10C,H10D), C11T(H11C,H11D), C12T(H12E,H12F), C6(H6B,H6A),
C6A(H6AA,H6AB), C12(H12A,H12B), C18(H18A,H18B), C24(H24A,H24B),
C30(H30A,H30B)
7.b Aromatic/amide H refined with riding coordinates:
C1(H1A), C1(H1B), C2(H2), C2A(H2A), C3(H3), C3A(H3A), C4(H4), C4A(H4A),
C7(H7), C8(H8), C9(H9), C10(H10), C13(H13), C14(H14), C15(H15), C16(H16),
C19(H19), C20(H20), C21(H21), C22(H22), C25(H25), C26(H26), C27(H27), C28(H28)
7.c Idealised Me refined as rotating group:
C31(H31A,H31B,H31C), C32(H32A,H32B,H32C), C33(H33A,H33B,H33C),
C34(H34A,H34B,
H34C), C35(H35A,H35B,H35C), C36(H36A,H36B,H36C)
This report has been created with Olex2, compiled on 2018.05.29 svn.r3508 for OlexSys.
Please let us know if there are any errors or if you would like to have additional features.

5·2 THF

Table S14 Crystal data and structure refinement for 5·2THF.

Empirical formula	$C_{128}H_{220}Ca_4Mn_5N_{18}O_{17}Si_{12}$
Formula weight	3055.31
Temperature/K	99.91
Crystal system	triclinic
Space group	P-1
a/Å	19.429(2)
b/Å	22.050(2)
c/Å	23.108(3)
α/°	87.300(2)
β/°	66.466(2)
γ/°	71.707(2)
Volume/Å^3	8582.9(16)
Z	2
ρ_{calc}g/cm^3	1.182
μ/mm^{-1}	0.617
F(000)	3246.0
Crystal size/mm^3	0.32 × 0.28 × 0.26
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.954 to 49.656
Index ranges	$-22 \leq h \leq 22$, $-25 \leq k \leq 25$, $-26 \leq l \leq 27$
Reflections collected	109187
Independent reflections	28380 [R_{int} = 0.0495, R_{sigma} = 0.0800]
Data/restraints/parameters	28380/1528/2007
Goodness-of-fit on F^2	1.355
Final R indexes [I>=2σ (I)]	R_1 = 0.1322, wR_2 = 0.3734
Final R indexes [all data]	R_1 = 0.2008, wR_2 = 0.4088
Largest diff. peak/hole / e Å^{-3}	3.25/-1.57

Table S15 Bond Lengths for 5·2THF.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	O1	2.166(6)	C65	C66	1.516(16)
Mn1	O2	2.167(5)	C71	C72	1.388(13)
Mn1	O10	2.208(5)	C72	C73	1.390(14)
Mn1	O11	2.249(5)	C73	C74	1.406(13)
Mn1	N1	2.283(8)	C74	C75	1.424(12)
Mn1	N2	2.302(7)	C75	C76	1.490(11)
Mn2	O3	2.117(6)	C81	C82	1.363(16)
Mn2	O4	2.149(7)	C82	C83	1.396(16)
Mn2	O7	2.239(5)	C83	C84	1.340(14)
Mn2	O12	2.257(5)	C84	C85	1.370(13)
Mn2	N3	2.328(8)	C85	C86	1.529(13)
Mn2	N4	2.279(8)	C91	C92	1.345(13)
Mn3	O5	2.174(6)	C92	C93	1.376(13)
Mn3	O6	2.190(6)	C93	C94	1.359(12)
Mn3	O8	2.261(5)	C94	C95	1.367(12)
Mn3	O9	2.258(5)	C95	C96	1.509(11)
Mn3	N5	2.348(8)	C106	C105	1.492(14)
Mn3	N6	2.305(10)	C116	C115	1.487(11)
Ca1	O4	2.326(6)	C121	C122	1.342(15)
Ca1	O5	2.335(6)	C122	C123	1.333(17)
Ca1	O7	2.397(6)	C123	C124	1.386(18)
Ca1	O8	2.374(5)	C124	C125	1.438(15)
Ca1	O13	2.479(6)	C125	C126	1.453(12)
Ca1	N7	2.615(7)	C131	C132	1.503(15)
Ca1	N8	2.648(8)	C132	C133	1.490(16)
Ca2	O1	2.312(6)	C133	C134	1.506(14)
Ca2	O6	2.297(6)	C141	C142	1.570(17)
Ca2	O9	2.387(5)	C144	C143	1.542(17)
Ca2	O10	2.405(5)	C151	C152	1.483(15)
Ca2	O14	2.460(6)	C152	C153	1.490(17)
Ca2	N9	2.638(7)	C153	C154	1.513(14)
Ca2	N10	2.596(7)	Mn4	N16	2.029(9)
Ca3	O2	2.286(6)	Mn4	N17	2.068(5)
Ca3	O3	2.306(6)	Mn4	N18	2.123(10)
Ca3	O11	2.382(5)	Si1	N16	1.660(9)
Ca3	O12	2.370(5)	Si1	C161	1.879(12)
Ca3	O15	2.464(6)	Si1	C162	1.871(13)
Ca3	N11	2.615(7)	Si1	C163	1.887(15)
Ca3	N12	2.569(7)	Si2	N16	1.740(10)

Ca04	O7	2.330(5)	Si2	C164	1.83(2)
Ca04	O8	2.313(5)	Si2	C165	1.93(2)
Ca04	O9	2.326(5)	Si2	C166	1.81(2)
Ca04	O10	2.325(5)	Si3	N17	1.6799(10)
Ca04	O11	2.321(5)	Si3	C174	1.8598(10)
Ca04	O12	2.335(5)	Si3	C175	1.8600(10)
O1	C16	1.338(11)	Si3	C176	1.8603(10)
O2	C26	1.388(10)	Si4A	N17	1.6799(10)
O3	C36	1.386(11)	Si4A	C71A	1.8602(11)
O4	C46	1.367(12)	Si4A	C72A	1.8600(11)
O5	C56	1.413(11)	Si4A	C73A	1.897(17)
O6	C66	1.373(12)	Si5	N18	1.660(8)
O7	C76	1.376(9)	Si5	C81A	1.8607(10)
O8	C86	1.414(10)	Si5	C82A	1.847(17)
O9	C96	1.416(9)	Si5	C83A	1.870(18)
O10	C106	1.404(9)	Si5	C181	1.819(14)
O11	C116	1.397(9)	Si5	C182	1.852(16)
O12	C126	1.413(9)	Si5	C183	1.944(15)
O13	C131	1.434(11)	Si6	N18	1.665(10)
O13	C134	1.440(11)	Si6	C184	1.811(14)
O14	C141	1.432(11)	Si6	C185	1.832(15)
O14	C144	1.483(11)	Si6	C186	1.927(13)
O15	C151	1.430(12)	N17	Si4	1.6801(10)
O15	C154	1.419(11)	Mn5	N19	2.061(9)
N1	C11	1.351(13)	Mn5	N20	2.195(10)
N1	C15	1.282(12)	Mn5	N21	1.986(8)
N2	C21	1.348(11)	Si	N20	1.701(14)
N2	C25	1.351(11)	Si	C9	1.875(15)
N3	C31	1.341(13)	Si	C10	1.897(16)
N3	C35	1.305(12)	Si	C206	1.913(16)
N4	C41	1.278(13)	Si7A	N19	1.724(9)
N4	C45	1.303(15)	Si7A	C3	1.889(13)
N5	C51	1.331(13)	Si7A	C4	1.872(13)
N5	C55	1.349(13)	Si7A	C5	1.918(15)
N6	C61	1.358(14)	Si8A	N19	1.668(10)
N6	C65	1.325(14)	Si8A	C1	1.881(14)
N7	C71	1.351(11)	Si8A	C2	1.887(15)
N7	C75	1.345(11)	Si8A	C196	1.882(12)
N8	C81	1.317(12)	Si9A	N20	1.727(13)
N8	C85	1.316(11)	Si9A	C6	1.961(14)
N9	C91	1.339(11)	Si9A	C7	1.850(15)
N9	C95	1.324(10)	Si9A	C8	1.824(16)

N10	C1A	1.366(16)	Si11	N21	1.643(9)
N10	C5A	1.327(16)	Si11	C211	1.886(15)
N10	C101	1.364(15)	Si11	C212	1.923(14)
N10	C105	1.297(15)	Si11	C213	1.849(14)
N11	C11A	1.336(17)	Si12	N21	1.709(9)
N11	C15A	1.326(17)	Si12	C214	1.811(11)
N11	C111	1.363(14)	Si12	C215	1.816(15)
N11	C115	1.315(13)	Si12	C216	1.808(10)
N12	C121	1.323(11)	N19	Si7	1.729(13)
N12	C125	1.331(12)	N19	Si8	1.689(14)
C1A	C2A	1.389(17)	N20	Si9	1.634(14)
C2A	C3A	1.406(17)	N20	Si10	1.710(16)
C3A	C4A	1.389(17)	C196	Si8	1.884(16)
C4A	C5A	1.407(17)	C206	Si10	1.864(18)
C5A	C106	1.513(16)	Si4	C171	1.8602(10)
C11	C12	1.396(19)	Si4	C172	1.8601(10)
C11A	C12A	1.380(14)	Si4	C173	1.8602(11)
C12	C13	1.347(19)	Si7	C191	1.849(18)
C12A	C13A	1.395(14)	Si7	C192	1.882(17)
C13	C14	1.353(15)	Si7	C193	1.922(18)
C13A	C14A	1.383(14)	Si8	C194	1.879(14)
C14	C15	1.340(13)	Si8	C195	1.827(17)
C14A	C15A	1.391(13)	Si9	C201	1.871(17)
C15	C16	1.578(13)	Si9	C202	1.895(18)
C15A	C116	1.499(13)	Si9	C203	1.898(14)
C21	C22	1.343(14)	Si10	C204	1.868(17)
C22	C23	1.364(15)	Si10	C205	1.881(18)
C23	C24	1.362(14)	O1S	C1S	1.72(2)
C24	C25	1.367(13)	O1S	C4S	1.496(19)
C25	C26	1.518(13)	C1S	C2S	1.42(2)
C31	C32	1.409(15)	C2S	C3S	1.428(7)
C32	C33	1.324(16)	C3S	C4S	1.423(7)
C33	C34	1.357(16)	O2S	C5S	1.405(16)
C34	C35	1.373(13)	O2S	C8S	1.454(16)
C35	C36	1.548(14)	O2T	C5T	1.448(19)
C41	C42	1.316(16)	O2T	C8T	1.433(19)
C42	C43	1.324(18)	C5T	C6T	1.562(19)
C42A	C43A	1.560(19)	C6T	C7T	1.545(19)
C42A	C141	1.584(17)	C7T	C8T	1.538(19)
C43	C44	1.408(18)	C5S	C6S	1.484(17)
C43A	C144	1.551(18)	C6S	C7S	1.547(17)
C44	C45	1.378(17)	C7S	C8S	1.543(16)

C45	C46	1.529(16)	C101	C102	1.389(16)
C51	C52	1.334(16)	C102	C103	1.399(17)
C52	C53	1.311(17)	C103	C104	1.378(16)
C53	C54	1.457(18)	C104	C105	1.397(16)
C54	C55	1.354(15)	C111	C112	1.382(12)
C55	C56	1.529(15)	C112	C113	1.386(12)
C61	C62	1.281(19)	C113	C114	1.379(12)
C62	C63	1.30(2)	C114	C115	1.390(12)
C63	C64	1.49(2)	C142	C143	1.550(18)
C64	C65	1.359(16)			

Table S16 Bond Angles for 5·2 THF.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Mn1	O2	167.4(2)	C23	C24	C25	120.3(10)
O1	Mn1	O10	81.6(2)	N2	C25	C24	120.9(9)
O1	Mn1	O11	105.7(2)	N2	C25	C26	116.2(8)
O1	Mn1	N1	74.4(3)	C24	C25	C26	122.7(9)
O1	Mn1	N2	98.7(2)	O2	C26	C25	115.0(8)
O2	Mn1	O10	109.5(2)	N3	C31	C32	120.2(12)
O2	Mn1	O11	81.6(2)	C33	C32	C31	120.0(12)
O2	Mn1	N1	95.1(3)	C32	C33	C34	118.8(11)
O2	Mn1	N2	74.3(2)	C33	C34	C35	120.1(12)
O10	Mn1	O11	85.75(19)	N3	C35	C34	122.0(10)
O10	Mn1	N1	154.9(3)	N3	C35	C36	116.3(9)
O10	Mn1	N2	98.6(2)	C34	C35	C36	121.7(11)
O11	Mn1	N1	93.5(2)	O3	C36	C35	113.0(9)
O11	Mn1	N2	155.6(2)	N4	C41	C42	126.6(13)
N1	Mn1	N2	92.4(3)	C41	C42	C43	117.6(13)
O3	Mn2	O4	171.5(2)	C43A	C42A	C141	103.1(18)
O3	Mn2	O7	103.3(2)	C42	C43	C44	119.8(13)
O3	Mn2	O12	81.81(19)	C144	C43A	C42A	100.4(17)
O3	Mn2	N3	73.7(3)	C45	C44	C43	116.1(15)
O3	Mn2	N4	98.5(3)	N4	C45	C44	122.2(12)
O4	Mn2	O7	82.4(2)	N4	C45	C46	117.9(10)
O4	Mn2	O12	105.1(2)	C44	C45	C46	119.9(14)
O4	Mn2	N3	99.5(3)	O4	C46	C45	116.0(10)
O4	Mn2	N4	76.5(3)	N5	C51	C52	123.0(12)
O7	Mn2	O12	85.30(17)	C53	C52	C51	120.1(12)
O7	Mn2	N3	98.0(2)	C52	C53	C54	120.2(12)
O7	Mn2	N4	157.5(3)	C55	C54	C53	115.4(13)
O12	Mn2	N3	155.4(3)	N5	C55	C54	122.8(11)
O12	Mn2	N4	92.6(2)	N5	C55	C56	117.2(9)

N4	Mn2	N3	93.2(3)	C54	C55	C56	120.0(11)
O5	Mn3	O6	174.2(2)	O5	C56	C55	114.3(9)
O5	Mn3	O8	81.2(2)	C62	C61	N6	123.8(15)
O5	Mn3	O9	104.0(2)	C61	C62	C63	119.9(16)
O5	Mn3	N5	74.1(3)	C62	C63	C64	120.2(14)
O5	Mn3	N6	100.9(3)	C65	C64	C63	115.3(15)
O6	Mn3	O8	102.5(2)	N6	C65	C64	120.7(13)
O6	Mn3	O9	80.9(2)	N6	C65	C66	118.3(10)
O6	Mn3	N5	102.5(3)	C64	C65	C66	120.9(14)
O6	Mn3	N6	74.3(3)	O6	C66	C65	114.5(10)
O8	Mn3	N5	154.8(3)	N7	C71	C72	121.8(10)
O8	Mn3	N6	97.2(3)	C71	C72	C73	119.9(9)
O9	Mn3	O8	84.60(19)	C72	C73	C74	118.5(9)
O9	Mn3	N5	96.6(2)	C73	C74	C75	118.6(9)
O9	Mn3	N6	155.0(3)	N7	C75	C74	121.3(8)
N6	Mn3	N5	92.3(3)	N7	C75	C76	118.0(7)
O4	Ca1	O5	171.8(2)	C74	C75	C76	120.7(8)
O4	Ca1	O7	75.4(2)	O7	C76	C75	114.5(7)
O4	Ca1	O8	98.7(2)	N8	C81	C82	124.4(11)
O4	Ca1	O13	94.6(2)	C81	C82	C83	118.5(11)
O4	Ca1	N7	92.5(2)	C84	C83	C82	117.1(11)
O4	Ca1	N8	87.6(3)	C83	C84	C85	120.0(11)
O5	Ca1	O7	97.5(2)	N8	C85	C84	124.1(9)
O5	Ca1	O8	75.62(19)	N8	C85	C86	116.9(8)
O5	Ca1	O13	93.6(2)	C84	C85	C86	118.9(9)
O5	Ca1	N7	88.2(2)	O8	C86	C85	113.7(7)
O5	Ca1	N8	95.3(2)	N9	C91	C92	125.2(9)
O7	Ca1	O13	141.86(19)	C91	C92	C93	117.4(8)
O7	Ca1	N7	66.1(2)	C94	C93	C92	118.7(9)
O7	Ca1	N8	137.8(2)	C93	C94	C95	120.0(9)
O8	Ca1	O7	78.44(18)	N9	C95	C94	122.3(8)
O8	Ca1	O13	139.7(2)	N9	C95	C96	117.5(8)
O8	Ca1	N7	138.7(2)	C94	C95	C96	120.2(8)
O8	Ca1	N8	66.2(2)	O9	C96	C95	115.5(7)
O13	Ca1	N7	77.9(2)	O10	C106	C5A	117.4(9)
O13	Ca1	N8	76.6(2)	O10	C106	C105	114.2(9)
N7	Ca1	N8	154.5(3)	O11	C116	C15A	117.7(9)
O1	Ca2	O9	101.60(19)	O11	C116	C115	116.0(8)
O1	Ca2	O10	74.6(2)	N12	C121	C122	126.7(11)
O1	Ca2	O14	95.4(2)	C123	C122	C121	117.1(11)
O1	Ca2	N9	87.3(2)	C122	C123	C124	120.3(13)
O1	Ca2	N10	94.3(2)	C123	C124	C125	119.0(13)

O6	Ca2	O1	172.9(2)	N12	C125	C124	118.4(10)
O6	Ca2	O9	76.0(2)	N12	C125	C126	121.8(8)
O6	Ca2	O10	98.3(2)	C124	C125	C126	119.8(11)
O6	Ca2	O14	90.7(2)	O12	C126	C125	114.9(7)
O6	Ca2	N9	97.8(2)	O13	C131	C132	106.9(9)
O6	Ca2	N10	83.2(2)	C133	C132	C131	105.6(9)
O9	Ca2	O10	78.86(17)	C132	C133	C134	102.5(9)
O9	Ca2	O14	138.30(19)	O13	C134	C133	107.2(8)
O9	Ca2	N9	66.39(19)	O14	C141	C42A	106.1(11)
O9	Ca2	N10	136.2(2)	O14	C141	C142	106.6(11)
O10	Ca2	O14	142.72(19)	O14	C144	C43A	106.5(13)
O10	Ca2	N9	136.56(19)	O14	C144	C143	105.0(12)
O10	Ca2	N10	66.45(19)	O15	C151	C152	107.3(10)
O14	Ca2	N9	76.8(2)	C151	C152	C153	101.7(10)
O14	Ca2	N10	78.9(2)	C152	C153	C154	102.8(10)
N10	Ca2	N9	155.8(2)	O15	C154	C153	105.4(9)
O2	Ca3	O3	174.7(2)	N16	Mn4	N17	116.3(4)
O2	Ca3	O11	76.35(18)	N16	Mn4	N18	121.4(3)
O2	Ca3	O12	99.4(2)	N17	Mn4	N18	122.3(3)
O2	Ca3	O15	92.5(2)	N16	Si1	C161	109.1(5)
O2	Ca3	N11	98.6(2)	N16	Si1	C162	114.9(6)
O2	Ca3	N12	81.7(2)	N16	Si1	C163	114.8(5)
O3	Ca3	O11	100.79(19)	C161	Si1	C163	106.4(6)
O3	Ca3	O12	75.59(19)	C162	Si1	C161	105.7(7)
O3	Ca3	O15	92.5(2)	C162	Si1	C163	105.3(6)
O3	Ca3	N11	84.2(2)	N16	Si2	C164	117.4(9)
O3	Ca3	N12	97.7(2)	N16	Si2	C165	105.9(8)
O11	Ca3	O15	139.9(2)	N16	Si2	C166	108.6(7)
O11	Ca3	N11	66.9(2)	C164	Si2	C165	102.1(10)
O11	Ca3	N12	136.2(2)	C166	Si2	C164	99.7(13)
O12	Ca3	O11	78.92(18)	C166	Si2	C165	123.7(11)
O12	Ca3	O15	141.2(2)	N17	Si3	C174	117.4(6)
O12	Ca3	N11	136.0(2)	N17	Si3	C175	110.2(5)
O12	Ca3	N12	67.8(2)	N17	Si3	C176	111.6(4)
O15	Ca3	N11	77.2(2)	C174	Si3	C175	107.1(7)
O15	Ca3	N12	77.7(2)	C174	Si3	C176	105.8(6)
N12	Ca3	N11	154.9(2)	C175	Si3	C176	103.8(6)
O7	Ca04	Mn1	139.73(15)	N17	Si4A	C71A	109.1(8)
O7	Ca04	O12	81.51(17)	N17	Si4A	C72A	117.9(8)
O8	Ca04	Mn1	139.20(14)	N17	Si4A	C73A	109.7(7)
O8	Ca04	O7	81.02(19)	C71A	Si4A	C73A	106.3(9)
O8	Ca04	O9	81.93(18)	C72A	Si4A	C71A	107.2(9)

O8	Ca04	O10	98.94(19)	C72A	Si4A	C73A	106.1(8)
O8	Ca04	O11	178.95(19)	N18	Si5	C81A	109.2(14)
O8	Ca04	O12	100.01(19)	N18	Si5	C82A	110.8(18)
O9	Ca04	Mn1	90.27(13)	N18	Si5	C83A	109.4(13)
O9	Ca04	O7	99.85(18)	N18	Si5	C181	112.8(9)
O9	Ca04	O12	177.81(18)	N18	Si5	C182	117.9(13)
O10	Ca04	Mn1	40.26(13)	N18	Si5	C183	106.3(9)
O10	Ca04	O7	178.38(19)	C81A	Si5	C83A	106.2(17)
O10	Ca04	O9	81.75(18)	C82A	Si5	C81A	111.5(15)
O10	Ca04	O12	96.91(18)	C82A	Si5	C83A	109.5(18)
O11	Ca04	Mn1	41.27(13)	C181	Si5	C182	112.2(13)
O11	Ca04	O7	98.55(19)	C181	Si5	C183	107.9(10)
O11	Ca04	O9	97.21(18)	C182	Si5	C183	97.9(12)
O11	Ca04	O10	81.51(19)	N18	Si6	C184	115.3(6)
O11	Ca04	O12	80.86(18)	N18	Si6	C185	116.6(7)
O12	Ca04	Mn1	87.59(13)	N18	Si6	C186	110.9(5)
Mn1	O1	Ca2	103.5(3)	C184	Si6	C185	103.4(7)
C16	O1	Mn1	119.4(5)	C184	Si6	C186	104.2(6)
C16	O1	Ca2	135.1(5)	C185	Si6	C186	105.1(8)
Mn1	O2	Ca3	103.2(2)	Si1	N16	Mn4	122.3(5)
C26	O2	Mn1	119.2(5)	Si1	N16	Si2	121.1(6)
C26	O2	Ca3	136.3(5)	Si2	N16	Mn4	116.5(5)
Mn2	O3	Ca3	104.2(2)	Si3	N17	Mn4	117.1(2)
C36	O3	Mn2	121.1(6)	Si3	N17	Si4A	119.4(5)
C36	O3	Ca3	132.7(6)	Si3	N17	Si4	125.0(4)
Mn2	O4	Ca1	103.4(3)	Si4A	N17	Mn4	122.4(5)
C46	O4	Mn2	116.0(6)	Si4	N17	Mn4	115.9(3)
C46	O4	Ca1	138.0(6)	Si5	N18	Mn4	116.3(5)
Mn3	O5	Ca1	103.5(2)	Si5	N18	Si6	126.3(6)
C56	O5	Mn3	118.8(6)	Si6	N18	Mn4	117.4(4)
C56	O5	Ca1	134.0(6)	N19	Mn5	N20	115.4(4)
Mn3	O6	Ca2	103.9(3)	N21	Mn5	N19	122.9(4)
C66	O6	Mn3	118.1(6)	N21	Mn5	N20	121.2(4)
C66	O6	Ca2	136.0(6)	N20	Si	C9	114.9(12)
Mn2	O7	Ca1	98.5(2)	N20	Si	C10	112.3(13)
Mn2	O7	Ca04	96.89(18)	N20	Si	C206	108.6(9)
Ca04	O7	Ca1	99.7(2)	C9	Si	C10	109.3(12)
C76	O7	Mn2	114.0(4)	C9	Si	C206	109.0(13)
C76	O7	Ca1	119.8(4)	C10	Si	C206	102.0(12)
C76	O7	Ca04	123.1(4)	N19	Si7A	C3	121.1(7)
Mn3	O8	Ca1	99.6(2)	N19	Si7A	C4	112.3(7)
Mn3	O8	Ca04	96.9(2)	N19	Si7A	C5	110.4(8)

Ca04	O8	Ca1	100.9(2)	C3	Si7A	C5	101.1(10)
C86	O8	Mn3	113.8(5)	C4	Si7A	C3	104.9(9)
C86	O8	Ca1	120.4(5)	C4	Si7A	C5	105.5(9)
C86	O8	Ca04	120.9(5)	N19	Si8A	C1	109.2(6)
Mn3	O9	Ca2	99.0(2)	N19	Si8A	C2	110.0(12)
Mn3	O9	Ca04	96.6(2)	N19	Si8A	C196	110.2(6)
Ca04	O9	Ca2	99.94(19)	C1	Si8A	C2	113.0(12)
C96	O9	Mn3	112.3(4)	C1	Si8A	C196	108.6(8)
C96	O9	Ca2	120.8(5)	C196	Si8A	C2	105.8(12)
C96	O9	Ca04	123.2(4)	N20	Si9A	C6	101.7(8)
Mn1	O10	Ca2	99.3(2)	N20	Si9A	C7	116.5(12)
Mn1	O10	Ca04	96.85(19)	N20	Si9A	C8	116.1(12)
Ca04	O10	Ca2	99.45(19)	C7	Si9A	C6	108.4(11)
C106	O10	Mn1	114.7(4)	C8	Si9A	C6	112.8(13)
C106	O10	Ca2	119.4(4)	C8	Si9A	C7	101.6(11)
C106	O10	Ca04	122.6(4)	N21	Si11	C211	113.1(5)
Mn1	O11	Ca3	97.81(19)	N21	Si11	C212	117.7(6)
Mn1	O11	Ca04	95.84(19)	N21	Si11	C213	110.7(6)
Ca04	O11	Ca3	100.1(2)	C211	Si11	C212	102.0(8)
C116	O11	Mn1	117.0(5)	C213	Si11	C211	108.8(8)
C116	O11	Ca3	120.1(4)	C213	Si11	C212	103.8(7)
C116	O11	Ca04	121.1(4)	N21	Si12	C214	113.4(6)
Mn2	O12	Ca3	98.02(19)	N21	Si12	C215	102.9(10)
Mn2	O12	Ca04	96.26(19)	N21	Si12	C216	109.5(6)
Ca04	O12	Ca3	100.0(2)	C214	Si12	C215	108.3(11)
C126	O12	Mn2	115.9(4)	C216	Si12	C214	108.3(7)
C126	O12	Ca3	119.2(4)	C216	Si12	C215	114.5(10)
C126	O12	Ca04	122.5(4)	Si7A	N19	Mn5	110.5(5)
C131	O13	Ca1	126.3(5)	Si8A	N19	Mn5	121.6(5)
C131	O13	C134	108.8(7)	Si8A	N19	Si7A	126.1(6)
C134	O13	Ca1	124.5(5)	Si7	N19	Mn5	124.2(6)
C141	O14	Ca2	124.5(5)	Si8	N19	Mn5	113.8(8)
C141	O14	C144	110.1(6)	Si8	N19	Si7	121.4(9)
C144	O14	Ca2	125.3(5)	Si	N20	Mn5	120.0(7)
C151	O15	Ca3	126.3(5)	Si	N20	Si9A	123.7(8)
C154	O15	Ca3	124.8(6)	Si9A	N20	Mn5	116.2(6)
C154	O15	C151	108.8(7)	Si9	N20	Mn5	120.6(8)
C11	N1	Mn1	122.1(8)	Si9	N20	Si10	120.8(10)
C15	N1	Mn1	115.7(6)	Si10	N20	Mn5	116.8(8)
C15	N1	C11	122.0(10)	Si11	N21	Mn5	117.5(5)
C21	N2	Mn1	127.4(6)	Si11	N21	Si12	127.1(5)
C21	N2	C25	117.3(8)	Si12	N21	Mn5	114.9(4)

C25	N2	Mn1	115.3(6)	N17	Si4	C171	109.7(7)
C31	N3	Mn2	125.8(8)	N17	Si4	C172	112.0(6)
C35	N3	Mn2	115.3(6)	N17	Si4	C173	115.9(6)
C35	N3	C31	118.9(9)	C171	Si4	C172	107.6(7)
C41	N4	Mn2	128.7(9)	C171	Si4	C173	105.6(7)
C41	N4	C45	117.7(10)	C172	Si4	C173	105.5(7)
C45	N4	Mn2	112.7(7)	N19	Si7	C191	114.1(19)
C51	N5	Mn3	127.3(8)	N19	Si7	C192	103.5(16)
C51	N5	C55	118.4(10)	N19	Si7	C193	103.2(16)
C55	N5	Mn3	113.9(6)	C191	Si7	C192	125.9(16)
C61	N6	Mn3	126.0(11)	C191	Si7	C193	108.0(16)
C65	N6	Mn3	114.1(7)	C192	Si7	C193	99.1(16)
C65	N6	C61	119.8(12)	N19	Si8	C196	109.2(10)
C71	N7	Ca1	125.8(7)	N19	Si8	C194	96.2(9)
C75	N7	Ca1	114.4(5)	N19	Si8	C195	114.6(19)
C75	N7	C71	119.7(8)	C194	Si8	C196	111.3(14)
C81	N8	Ca1	128.7(7)	C195	Si8	C196	111.1(14)
C85	N8	Ca1	115.5(6)	C195	Si8	C194	113.5(16)
C85	N8	C81	115.7(9)	N20	Si9	C201	121.1(15)
C91	N9	Ca2	127.8(6)	N20	Si9	C202	107.3(15)
C95	N9	Ca2	115.9(5)	N20	Si9	C203	104.5(13)
C95	N9	C91	116.3(8)	C201	Si9	C202	107.9(14)
C1A	N10	Ca2	126.0(12)	C201	Si9	C203	110.0(16)
C5A	N10	Ca2	115.4(9)	C202	Si9	C203	104.9(17)
C5A	N10	C1A	114.7(14)	N20	Si10	C206	110.5(11)
C101	N10	Ca2	123.7(11)	N20	Si10	C204	106.3(14)
C105	N10	Ca2	115.7(8)	N20	Si10	C205	111.5(19)
C105	N10	C101	120.5(13)	C206	Si10	C204	110.7(17)
C11A	N11	Ca3	122.7(13)	C206	Si10	C205	106.5(17)
C15A	N11	Ca3	115.1(9)	C204	Si10	C205	111.3(17)
C15A	N11	C11A	120.1(16)	C4S	O1S	C1S	95.3(13)
C111	N11	Ca3	128.1(9)	C2S	C1S	O1S	105.6(13)
C115	N11	Ca3	114.7(6)	C1S	C2S	C3S	108.8(14)
C115	N11	C111	116.9(11)	C4S	C3S	C2S	110.3(13)
C121	N12	Ca3	128.2(7)	C3S	C4S	O1S	112.1(14)
C121	N12	C125	118.3(8)	C5S	O2S	C8S	108.3(14)
C125	N12	Ca3	112.8(5)	C8T	O2T	C5T	107(2)
N10	C1A	C2A	124.6(19)	O2T	C5T	C6T	102(2)
C1A	C2A	C3A	119.6(18)	C7T	C6T	C5T	103.8(19)
C4A	C3A	C2A	115.8(17)	C8T	C7T	C6T	101.8(17)
C3A	C4A	C5A	119.9(17)	O2T	C8T	C7T	109.9(18)
N10	C5A	C4A	124.7(14)	O2S	C5S	C6S	115.0(17)

N10	C5A	C106	115.9(13)	C5S	C6S	C7S	96.9(16)
C4A	C5A	C106	119.2(14)	C8S	C7S	C6S	107.3(14)
N1	C11	C12	117.5(13)	O2S	C8S	C7S	101.8(13)
N11	C11A	C12A	123(2)	N10	C101	C102	120.4(17)
C13	C12	C11	120.9(13)	C101	C102	C103	118.0(16)
C11A	C12A	C13A	117.6(19)	C104	C103	C102	120.5(15)
C12	C13	C14	117.0(13)	C103	C104	C105	117.1(16)
C14A	C13A	C12A	117.8(19)	N10	C105	C106	119.3(13)
C15	C14	C13	122.1(11)	N10	C105	C104	123.2(13)
C13A	C14A	C15A	121(2)	C104	C105	C106	117.4(13)
N1	C15	C14	120.5(9)	N11	C111	C112	123.3(15)
N1	C15	C16	116.7(9)	C111	C112	C113	118.0(15)
C14	C15	C16	122.7(10)	C114	C113	C112	119.1(14)
N11	C15A	C14A	119.3(15)	C113	C114	C115	118.5(14)
N11	C15A	C116	117.4(14)	N11	C115	C116	119.0(10)
C14A	C15A	C116	123.2(17)	N11	C115	C114	123.6(11)
O1	C16	C15	113.4(8)	C114	C115	C116	116.8(12)
C22	C21	N2	123.3(10)	C143	C142	C141	100.1(17)
C21	C22	C23	119.2(10)	C144	C143	C142	103.3(13)
C24	C23	C22	118.8(10)				

Table S17 Solvent masks information for 5·2 THF.

Number	X	Y	Z	Volume	Electron count	Content
1	0.500	0.000	1.000	827	215	
2	0.240	0.819	0.904	10	1	
3	0.760	0.181	0.096	11	1	

Experimental

A single crystal of $C_{128}H_{220}Ca_4Mn_5N_{18}O_{17}Si_{12}$ was selected and mounted on a diffractometer. The crystal was kept at 99.91 K during data collection. The structure was solved with SHELXS and refined with the SHELX refinement package using least squares minimization and OLEX2 [1] as a GUI.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

Crystal structure determination of 5·2 THF

Crystal Data for $C_{128}H_{220}Ca_4Mn_5N_{18}O_{17}Si_{12}$ (M =3055.31 g/mol): triclinic, space group P-1 (no. 2), a = 19.429(2) Å, b = 22.050(2) Å, c = 23.108(3) Å, α = 87.300(2)°, β = 66.466(2)°, γ = 71.707(2)°, V = 8582.9(16) Å^3, Z = 2, T = 99.91 K, μ(MoKα) = 0.617 mm^{-1}, $Dcalc$ = 1.182 g/cm^3, 109187 reflections measured (1.954° ≤ 2Θ ≤ 49.656°), 28380 unique (R_{int} = 0.0495, R_{sigma} = 0.0800) which were used in all calculations. The final R_1 was 0.1322 (I > 2σ(I)) and wR_2 was 0.4088 (all data).

Refinement model description

Number of restraints - 1528, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All C(H,H) groups, All C(H,H,H,H) groups

At 1.5 times of:

All C(H,H,H) groups, All C(H,H,H,H,H,H) groups

2. Restrained distances

C203-Si9

1.86 with sigma of 0.02

Si8-C194

1.86 with sigma of 0.02

N10-C1A = N10-C101 = N10-C5A = N10-C105

1.33 with sigma of 0.02

C105-C104 = C5A-C4A = C104-C103 = C4A-C3A = C103-C102 = C3A-C2A = C102-C101 = C2A-C1A

1.39 with sigma of 0.02

C5A-C106 = C106-C105

1.5 with sigma of 0.02

C11A-C12A = C112-C111 = C13A-C12A = C113-C112 = C14A-C13A = C114-C113 = C15A-C14A = C115-C114

1.39 with sigma of 0.02

C116-C15A = C116-C115

1.5 with sigma of 0.02

N11-C11A = N11-C111 = N11-C15A = N11-C115

1.33 with sigma of 0.02

C12A-C11A = C112-C111 = C13A-C12A = C113-C112 = C14A-C13A = C114-C113 = C15A-C14A = C115-C114

1.39 with sigma of 0.02

C15A-C116 = C116-C115

1.5 with sigma of 0.02

C141-C42A = C142-C141 = C42A-C43A = C143-C142 = C144-C143 = C144-C43A

1.55 with sigma of 0.02

Mn5-N19

2.05 with sigma of 0.02

Si7-N19 = Si7A-N19 = Si8-N19 = Si8A-N19

1.68 with sigma of 0.02

Si7A-C4 = Si7-C192 = Si7A-C5 = Si7-C193 = Si7A-C3 = Si7-C191 = Si8A-C2 = Si8-C195 = Si8A-C1 = Si8A-C196 = Si8-C194 = Si8-C196

1.86 with sigma of 0.02

Mn5-N20

2.05 with sigma of 0.02

Si9A-N20 = Si9-N20 = Si-N20 = Si10-N20

1.68 with sigma of 0.02

Si9A-C6 = Si9-C203 = Si9A-C7 = Si9-C201 = Si9A-C8 = Si9-C202 = Si-C9 = Si10-

C204 = Si-C10 = Si10-C205 = Si10-C206 = Si-C206
1.86 with sigma of 0.02
Mn5-N21
2.05 with sigma of 0.02
Si12-N21 = Si11-N21
1.68 with sigma of 0.02
Si12-C216 = Si12-C215 = Si12-C214
1.68 with sigma of 0.02
Mn4-N17
2.05 with sigma of 0.02
Si4A-N17 = Si4-N17 = Si3-N17
1.68 with sigma of 0.001
Si4A-C72A = Si4A-C71A = Si4-C171 = Si4-C172 = Si4-C173 = Si3-C175 = Si3-C176 = Si3-C174
1.86 with sigma of 0.001
C81A-Si5 = Si5-C182 = Si5-C82A = Si5-C183 = Si5-C83A = Si5-C181
1.86 with sigma of 0.02
Si5-C81A
1.86 with sigma of 0.001
O2T-C5T = O2S-C5S = O2T-C8T = O2S-C8S
1.45 with sigma of 0.02
C6T-C5T = C6S-C5S = C7T-C6T = C7S-C6S = C8T-C7T = C8S-C7S
1.54 with sigma of 0.02
C105-C101
2.3 with sigma of 0.04
C105-C103
2.41 with sigma of 0.04
C104-C102
2.41 with sigma of 0.04
C103-C101
2.41 with sigma of 0.04
C111-C115
2.3 with sigma of 0.04
C111-C113
2.41 with sigma of 0.04
C112-C114
2.41 with sigma of 0.04
C113-C115
2.41 with sigma of 0.04
C195-C194
3.04 with sigma of 0.04
Si7-Si8
2.9 with sigma of 0.04
C191-C192
3.1 with sigma of 0.04
C192-C193

3.1 with sigma of 0.04
C193-C191
3.1 with sigma of 0.04
C194-C195
3.1 with sigma of 0.04
Si9-Si10
2.9 with sigma of 0.04
C203-C201
3.1 with sigma of 0.04
C201-C202
3.1 with sigma of 0.04
C202-C203
3.1 with sigma of 0.04
C204-C205
3.1 with sigma of 0.04
Si8-Si7
3 with sigma of 0.01
C183-C182
3.03 with sigma of 0.04
C182-C181
3.03 with sigma of 0.04
C181-C183
3.03 with sigma of 0.04
C172-C173
3.04 with sigma of 0.02
C173-C171
3.04 with sigma of 0.02
C171-C172
3.04 with sigma of 0.02
C5S-C8S
2.29 with sigma of 0.04
O2S-C6S
2.44 with sigma of 0.04
O2S-C7S
2.44 with sigma of 0.04
C6S-C8S
2.52 with sigma of 0.04
C5A-C1A
2.3 with sigma of 0.04
N10-C4A
2.36 with sigma of 0.04
N10-C104
2.36 with sigma of 0.04
N10-C2A
2.36 with sigma of 0.04
N10-C102

2.36 with sigma of 0.04
C5A-C3A
2.41 with sigma of 0.04
C4A-C2A
2.41 with sigma of 0.04
C3A-C1A
2.41 with sigma of 0.04
C11A-C15A
2.3 with sigma of 0.04
N11-C112
2.36 with sigma of 0.04
N11-C12A
2.36 with sigma of 0.04
N11-C14A
2.36 with sigma of 0.04
N11-C114
2.36 with sigma of 0.04
C11A-C13A
2.41 with sigma of 0.04
C12A-C14A
2.41 with sigma of 0.04
C13A-C15A
2.41 with sigma of 0.04
O14-C42A
2.44 with sigma of 0.04
O14-C142
2.44 with sigma of 0.04
O14-C143
2.44 with sigma of 0.04
O14-C43A
2.44 with sigma of 0.04
C141-C143
2.52 with sigma of 0.04
C141-C43A
2.52 with sigma of 0.04
C144-C42A
2.52 with sigma of 0.04
C144-C142
2.52 with sigma of 0.04
Mn5-Si9
3.23 with sigma of 0.04
Mn5-Si
3.23 with sigma of 0.04
Mn5-Si10
3.23 with sigma of 0.04
C194-C196

3.04 with sigma of 0.04
C196-C195
3.04 with sigma of 0.04
Mn5-Si7
3.23 with sigma of 0.04
Mn5-Si8A
3.23 with sigma of 0.04
Mn5-Si8
3.23 with sigma of 0.04
Si7A-Si8A
2.9 with sigma of 0.04
C5-C4
3.1 with sigma of 0.04
C4-C3
3.1 with sigma of 0.04
C3-C5
3.1 with sigma of 0.04
C196-C194
3.1 with sigma of 0.04
C195-C196
3.1 with sigma of 0.04
C196-C2
3.1 with sigma of 0.04
C2-C1
3.1 with sigma of 0.04
C1-C196
3.1 with sigma of 0.04
N19-C195
2.9 with sigma of 0.04
N19-C194
2.9 with sigma of 0.04
N19-C2
2.9 with sigma of 0.04
N19-C1
2.9 with sigma of 0.04
N19-C196
2.9 with sigma of 0.04
N19-C191
2.9 with sigma of 0.04
N19-C192
2.9 with sigma of 0.04
N19-C193
2.9 with sigma of 0.04
N19-C5
2.9 with sigma of 0.04
N19-C4

2.9 with sigma of 0.04
N19-C3
2.9 with sigma of 0.04
Mn5-Si7A
3.3 with sigma of 0.04
Mn5-Si9A
3.23 with sigma of 0.04
Si9A-Si
2.9 with sigma of 0.04
N20-C6
2.9 with sigma of 0.04
N20-C7
2.9 with sigma of 0.04
N20-C8
2.9 with sigma of 0.04
N20-C203
2.9 with sigma of 0.04
N20-C201
2.9 with sigma of 0.04
N20-C202
2.9 with sigma of 0.04
N20-C9
2.9 with sigma of 0.04
N20-C10
2.9 with sigma of 0.04
N20-C204
2.9 with sigma of 0.04
N20-C205
2.9 with sigma of 0.04
N20-C206
2.9 with sigma of 0.04
C6-C7
3.1 with sigma of 0.04
C7-C8
3.1 with sigma of 0.04
C8-C6
3.1 with sigma of 0.04
C9-C10
3.1 with sigma of 0.04
C10-C206
3.1 with sigma of 0.04
C206-C9
3.1 with sigma of 0.04
C205-C206
3.1 with sigma of 0.04
C206-C204

3.1 with sigma of 0.04
Mn5-Si12
3.23 with sigma of 0.04
Si12-Si11
2.9 with sigma of 0.04
N21-C215
2.9 with sigma of 0.04
N21-C214
2.9 with sigma of 0.04
N21-C216
2.9 with sigma of 0.04
C216-C215
3.1 with sigma of 0.04
C215-C214
3.1 with sigma of 0.04
C214-C216
3.1 with sigma of 0.04
N18-C83A
2.9 with sigma of 0.04
N18-C183
2.9 with sigma of 0.04
N18-C82A
2.9 with sigma of 0.04
N18-C81A
2.9 with sigma of 0.04
N18-C181
2.9 with sigma of 0.04
C83A-C82A
3.03 with sigma of 0.04
C82A-C81A
3.03 with sigma of 0.04
C81A-Si5 = C81A-C82A
3.03 with sigma of 0.04
Mn4-Si4A
3.24 with sigma of 0.04
Mn4-Si4
3.24 with sigma of 0.04
Mn4-Si3
3.24 with sigma of 0.04
Si4-Si3
2.91 with sigma of 0.02
N17-C71A
2.9 with sigma of 0.02
N17-C72A
2.9 with sigma of 0.02
N17-C73A

2.9 with sigma of 0.02
N17-C171
2.9 with sigma of 0.02
N17-C172
2.9 with sigma of 0.02
N17-C173
2.9 with sigma of 0.02
N17-C176
2.9 with sigma of 0.02
N17-C174
2.9 with sigma of 0.02
N17-C175
2.9 with sigma of 0.02
C72A-C71A
3.04 with sigma of 0.02
C72A-C73A
3.04 with sigma of 0.02
C73A-C71A
3.04 with sigma of 0.02
C176-C174
3.04 with sigma of 0.02
C176-C175
3.04 with sigma of 0.02
C175-C174
3.04 with sigma of 0.02
C165-C164
3.1 with sigma of 0.04
C5T-C8T
2.29 with sigma of 0.04
O2T-C6T
2.44 with sigma of 0.04
O2T-C7T
2.44 with sigma of 0.04
C5T-C7T
2.52 with sigma of 0.04
C6T-C8T
2.52 with sigma of 0.04
C5S-C7T
2.52 with sigma of 0.04
3. Restrained planarity
N10, C1A, C2A, C3A, C4A, C5A, C106
with sigma of 0.1
N10, C106, C101, C102, C103, C104, C105
with sigma of 0.1
N11, C116, C111, C112, C113, C114, C115
with sigma of 0.1

N11, C11A, C12A, C13A, C14A, C15A, C116
with sigma of 0.1
Mn5, N19, Si7, Si8
with sigma of 0.1
Mn5, Si11, Si12, N21
with sigma of 0.1
4. Rigid bond restraints
N10, C1A, C2A, C3A, C4A, C5A, C106, C101, C102, C103, C104, C105
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
N11, C11A, C12A, C13A, C14A, C15A, C116, C111, C112, C113, C114, C115
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
C42A, C43A, C142, C143
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
Si7A, Si8A, N19, C1, C2, C3, C4, C5, C196, Si7, Si8, C191, C192, C193, C194, C195
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
Si, Si9A, N20, C6, C7, C8, C9, C10, C206, Si9, Si10, C201, C202, C203, C204, C205
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
Si5, C81A, C82A, C83A, C181, C182, C183
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
Si3, Si4A, N17, C174, C175, C176, Si4, C171, C172, C173
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
Si4A, N17, C71A, C72A, C73A, Si4, C171, C172, C173
with sigma for 1-2 distances of 0.003 and sigma for 1-3 distances of 0.003
O2S, O2T, C5T, C6T, C7T, C8T, C5S, C6S, C7S, C8S
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
5. Uiso/Uaniso restraints and constraints
N10 ≈ C1A ≈ C2A ≈ C3A ≈ C4A ≈ C5A ≈ C106 ≈ C101 ≈ C102 ≈ C103 ≈ C104 ≈ C105: within 2A with sigma of 0.04 and sigma for terminal atoms of 0.08
N11 ≈ C11A ≈ C12A ≈ C13A ≈ C14A ≈ C15A ≈ C116 ≈ C111 ≈ C112 ≈ C113 ≈ C114 ≈ C115: within 2A with sigma of 0.04 and sigma for terminal atoms of 0.08
C42A ≈ C43A ≈ C142 ≈ C143: within 2A with sigma of 0.04 and sigma for terminal atoms of 0.08
Si7A ≈ Si8A ≈ N19 ≈ C1 ≈ C2 ≈ C3 ≈ C4 ≈ C5 ≈ C196 ≈ Si7 ≈ Si8 ≈ C191 ≈ C192 ≈ C193 ≈ C194 ≈ C195: within 2A with sigma of 0.04 and sigma for terminal atoms of 0.08
Si ≈ Si9A ≈ N20 ≈ C6 ≈ C7 ≈ C8 ≈ C9 ≈ C10 ≈ C206 ≈ Si9 ≈ Si10 ≈ C201 ≈ C202 ≈ C203 ≈ C204 ≈ C205: within 2A with sigma of 0.003 and sigma for terminal atoms of 0.02
Si5 ≈ C81A ≈ C82A ≈ C83A ≈ C181 ≈ C182 ≈ C183: within 2A with sigma of 0.04 and sigma for terminal atoms of 0.08
Si3 ≈ Si4A ≈ N17 ≈ C174 ≈ C175 ≈ C176 ≈ Si4 ≈ C171 ≈ C172 ≈ C173: within 2A with sigma of 0.04 and sigma for terminal

atoms of 0.08
Si4A ≈ N17 ≈ C71A ≈ C72A ≈ C73A ≈ Si4 ≈ C171 ≈ C172
≈ C173: within 2A with sigma of 0.003 and sigma for terminal atoms of 0.006
O2S ≈ O2T ≈ C5T ≈ C6T ≈ C7T ≈ C8T ≈ C5S ≈ C6S ≈
C7S ≈ C8S: within 2A with sigma of 0.04 and sigma for terminal atoms of 0.08
6. Others
Sof(C1A)=Sof(H1A)=Sof(C2A)=Sof(H2A)=Sof(C3A)=Sof(H3A)=Sof(C4A)=Sof(H4A)=
Sof(C5A)=Sof(H10C)=Sof(H10D)=1-FVAR(1)
Sof(H10A)=Sof(H10B)=Sof(C101)=Sof(H101)=Sof(C102)=Sof(H102)=Sof(C103)=
Sof(H103)=Sof(C104)=Sof(H104)=Sof(C105)=FVAR(1)
Sof(C11A)=Sof(H11A)=Sof(C12A)=Sof(H12A)=Sof(C13A)=Sof(H13A)=Sof(C14A)=
Sof(H14A)=Sof(C15A)=Sof(H11D)=Sof(H11E)=1-FVAR(2)
Sof(H11B)=Sof(H11C)=Sof(C111)=Sof(H111)=Sof(C112)=Sof(H112)=Sof(C113)=
Sof(H113)=Sof(C114)=Sof(H114)=Sof(C115)=FVAR(2)
Sof(C42A)=Sof(H42A)=Sof(H42B)=Sof(C43A)=Sof(H43A)=Sof(H43B)=Sof(H14D)=
Sof(H14E)=Sof(H14H)=Sof(H14I)=1-FVAR(3)
Sof(H14B)=Sof(H14C)=Sof(H14F)=Sof(H14G)=Sof(C142)=Sof(H14J)=Sof(H14K)=
Sof(C143)=Sof(H14L)=Sof(H14M)=FVAR(3)
Sof(C81A)=Sof(H81A)=Sof(H81B)=Sof(H81C)=Sof(C82A)=Sof(H82A)=Sof(H82B)=
Sof(H82C)=Sof(C83A)=Sof(H83A)=Sof(H83B)=Sof(H83C)=1-FVAR(4)
Sof(C181)=Sof(H18J)=Sof(H18K)=Sof(H18L)=Sof(C182)=Sof(H18M)=Sof(H18N)=
Sof(H18O)=Sof(C183)=Sof(H18P)=Sof(H18Q)=Sof(H18R)=FVAR(4)
Sof(Si4A)=Sof(C71A)=Sof(H71A)=Sof(H71B)=Sof(H71C)=Sof(C72A)=Sof(H72A)=
Sof(H72B)=Sof(H72C)=Sof(C73A)=Sof(H73A)=Sof(H73B)=Sof(H73C)=1-FVAR(5)
Sof(Si4)=Sof(C171)=Sof(H17J)=Sof(H17K)=Sof(H17L)=Sof(C172)=Sof(H17M)=
Sof(H17N)=Sof(H17O)=Sof(C173)=Sof(H17P)=Sof(H17Q)=Sof(H17R)=FVAR(5)
Sof(Si7A)=Sof(Si8A)=Sof(C1)=Sof(H1B)=Sof(H1C)=Sof(H1D)=Sof(C2)=Sof(H2B)=

Sof(H2C)=Sof(H2D)=Sof(C3)=Sof(H3B)=Sof(H3C)=Sof(H3D)=Sof(C4)=Sof(H4B)=Sof(H4C)
=
Sof(H4D)=Sof(C5)=Sof(H5A)=Sof(H5B)=Sof(H5C)=Sof(H19D)=Sof(H19E)=Sof(H19F)=1-
FVAR(6)
Sof(H19A)=Sof(H19B)=Sof(H19C)=Sof(Si7)=Sof(Si8)=Sof(C191)=Sof(H19G)=Sof(H19H)=
Sof(H19I)=Sof(C192)=Sof(H19J)=Sof(H19K)=Sof(H19L)=Sof(C193)=Sof(H19M)=
Sof(H19N)=Sof(H19O)=Sof(C194)=Sof(H19P)=Sof(H19Q)=Sof(H19R)=Sof(C195)=
Sof(H19S)=Sof(H19T)=Sof(H19U)=FVAR(6)
Sof(Si)=Sof(Si9A)=Sof(C6)=Sof(H6A)=Sof(H6B)=Sof(H6C)=Sof(C7)=Sof(H7A)=

Sof(H7B)=Sof(H7C)=Sof(C8)=Sof(H8A)=Sof(H8B)=Sof(H8C)=Sof(C9)=Sof(H9A)=Sof(H9B)
=
Sof(H9C)=Sof(C10)=Sof(H10E)=Sof(H10F)=Sof(H10G)=Sof(H20D)=Sof(H20E)=Sof(H20F)=
1-FVAR(7)
Sof(H20A)=Sof(H20B)=Sof(H20C)=Sof(Si9)=Sof(Si10)=Sof(C201)=Sof(H20G)=
Sof(H20H)=Sof(H20I)=Sof(C202)=Sof(H20J)=Sof(H20K)=Sof(H20L)=Sof(C203)=
Sof(H20M)=Sof(H20N)=Sof(H20O)=Sof(C204)=Sof(H20P)=Sof(H20Q)=Sof(H20R)=
Sof(C205)=Sof(H20S)=Sof(H20T)=Sof(H20U)=FVAR(7)

Sof(O2T)=Sof(C5T)=Sof(H5TA)=Sof(H5TB)=Sof(C6T)=Sof(H6TA)=Sof(H6TB)=Sof(C7T)=
Sof(H7TA)=Sof(H7TB)=Sof(C8T)=Sof(H8TA)=Sof(H8TB)=1-FVAR(8)
Sof(O2S)=Sof(C5S)=Sof(H5SA)=Sof(H5SB)=Sof(C6S)=Sof(H6SA)=Sof(H6SB)=Sof(C7S)=
Sof(H7SA)=Sof(H7SB)=Sof(C8S)=Sof(H8SA)=Sof(H8SB)=FVAR(8)
7.a Secondary CH2 refined with riding coordinates:
C16(H16A,H16B), C26(H26A,H26B), C36(H36A,H36B), C42A(H42A,H42B), C43A(H43A,
H43B), C46(H46A,H46B), C56(H56A,H56B), C66(H66A,H66B), C76(H76A,H76B),
C86(H86A,H86B), C96(H96A,H96B), C106(H10C,H10D), C106(H10A,H10B), C116(H11D,
H11E), C116(H11B,H11C), C126(H12B,H12C), C131(H13B,H13C), C132(H13D,H13E),
C133(H13F,H13G), C134(H13H,H13I), C141(H14D,H14E), C141(H14B,H14C), C144(H14H,
H14I), C144(H14F,H14G), C151(H15A,H15B), C152(H15C,H15D), C153(H15E,H15F),
C154(H15G,H15H), C1S(H1SA,H1SB), C2S(H2SA,H2SB), C3S(H3SA,H3SB), C4S(H4SA,
H4SB), C5T(H5TA,H5TB), C6T(H6TA,H6TB), C7T(H7TA,H7TB), C8T(H8TA,H8TB),
C5S(H5SA,H5SB), C6S(H6SA,H6SB), C7S(H7SA,H7SB), C8S(H8SA,H8SB), C142(H14J,
H14K), C143(H14L,H14M)
7.b Me refined with riding coordinates:
C71A(H71A,H71B,H71C), C72A(H72A,H72B,H72C), C73A(H73A,H73B,H73C),
C81A(H81A,
H81B,H81C), C82A(H82A,H82B,H82C), C83A(H83A,H83B,H83C),
C161(H16C,H16D,H16E),
C162(H16F,H16G,H16H), C163(H16I,H16J,H16K), C164(H16L,H16M,H16N), C165(H16O,
H16P,H16Q), C166(H16R,H16S,H16T), C174(H17A,H17B,H17C), C175(H17D,H17E,H17F),
C176(H17G,H17H,H17I), C184(H18A,H18B,H18C), C185(H18D,H18E,H18F), C186(H18G,
H18H,H18I), C1(H1B,H1C,H1D), C2(H2B,H2C,H2D), C3(H3B,H3C,H3D),
C4(H4B,H4C,H4D),
C5(H5A,H5B,H5C), C6(H6A,H6B,H6C), C7(H7A,H7B,H7C), C8(H8A,H8B,H8C), C9(H9A,
H9B,H9C), C10(H10E,H10F,H10G), C196(H19D,H19E,H19F), C196(H19A,H19B,H19C),
C206(H20D,H20E,H20F), C206(H20A,H20B,H20C), C211(H21A,H21B,H21C), C212(H21D,
H21E,H21F), C213(H21G,H21H,H21I), C214(H21J,H21K,H21L), C215(H21M,H21N,H21O),
C216(H21P,H21Q,H21R), C171(H17J,H17K,H17L), C172(H17M,H17N,H17O), C173(H17P,
H17Q,H17R), C181(H18J,H18K,H18L), C182(H18M,H18N,H18O), C183(H18P,H18Q,H18R),
C191(H19G,H19H,H19I), C192(H19J,H19K,H19L), C193(H19M,H19N,H19O), C194(H19P,
H19Q,H19R), C195(H19S,H19T,H19U), C201(H20G,H20H,H20I), C202(H20J,H20K,H20L),
C203(H20M,H20N,H20O), C204(H20P,H20Q,H20R), C205(H20S,H20T,H20U)
7.c Aromatic/amide H refined with riding coordinates:
C1A(H1A), C2A(H2A), C3A(H3A), C4A(H4A), C11(H11), C11A(H11A), C12(H12),
C12A(H12A), C13(H13), C13A(H13A), C14(H14), C14A(H14A), C21(H21), C22(H22),
C23(H23), C24(H24), C31(H31), C32(H32), C33(H33), C34(H34), C41(H41), C42(H42),
C43(H43), C44(H44), C51(H51), C52(H52), C53(H53), C54(H54), C61(H61),
C62(H62), C63(H63), C64(H64), C71(H71), C72(H72), C73(H73), C74(H74), C81(H81),
C82(H82), C83(H83), C84(H84), C91(H91), C92(H92), C93(H93), C94(H94),
C121(H121), C122(H122), C123(H123), C124(H124), C101(H101), C102(H102),
C103(H103), C104(H104), C111(H111), C112(H112), C113(H113), C114(H114)
This report has been created with Olex2, compiled on 2018.05.29 svn.r3508 for OlexSys.
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