Electronic Supplementary Material (ESI) for Dalton Transactions.

High-yield synthesis of a unique Mn(III) siloxide complex through $KMnO_4$ oxidation of a Mn(II) precursor

Volker Lorenz,[a] Sophie Ehle,[a] Phil Liebing,[b] Felix Engelhardt,[a] Haleh Hashemi-Haeri,[c] Florian Oehler,[d] Dariush Hinderberger,[c] Sabine Busse,[a] Jens Urbaschok[a] and Frank T. Edelmann

Supplementary Information

---

[a] Chemisches Institut der Otto-von-Guericke-Universität, 39106 Magdeburg, Germany.

[b] ETH Zürich, Laboratorium für Anorganische Chemie, Vladimir-Prelog-Weg 1-5/10, 8093 Zürich, Switzerland.

[c] Martin-Luther-Universität Halle-Wittenberg, Institut für Chemie - Physikalische Chemie, Von-Danckelmann-Platz 4, 06120 Halle (Saale), Germany.

[d] Martin-Luther-Universität Halle-Wittenberg, Institut für Chemie - Anorganische Chemie, Kurt-Mothes-Str. 2, 06120 Halle (Saale), Germany.

Table of Contents

1. NMR and UV vis measurements

NMR spectra:

Despite several attempts, no meaningful NMR data could be obtained for compounds **2** and **3**.

UV vis spectra:

The UV-vis measurements of compounds **1-3** were carried out an analytic Jena SPECORD 210plus with use of 10.0 mm quartz cells. Samples with concentrations of ca. 1 x 10^{-7} M in CH_3CN were measured against the solvent in the reference cell. The similarity of the spectra of **2** and **3** indicates that the manganese(III) species **3** decomposes in these highly diluted solutions (Fig. S1).

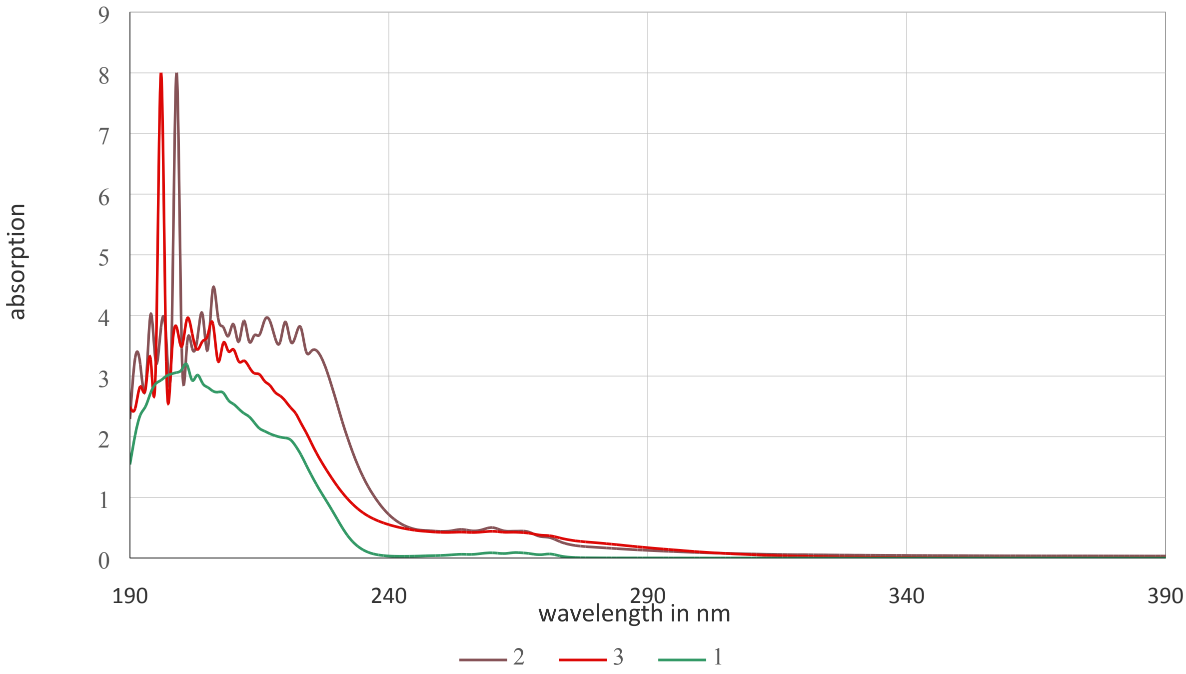

Fig. S1. UV-vis spectra of compound **1–3** measured in CH_3CN

2. Magnetic moments

The magnetic moments were determined with the Gouy method at 293 K, using the magnetic balance Johnson Matthey MSB MK I. Diamagnetic correction have been applied as $\chi_{mol,\ corr} = \chi_{mol} - \chi_{mol,\ dia}$ while $\chi_{mol,\ dia}$ was calculated as the sum of the molar diamagnetic susceptibility of each atom. The molar diamagnetic susceptibility values of the atoms were taken from literature [1] as $\chi^{O}_{mol,\ dia} = -4.61 \cdot 10^{-6}$ emu / mol, $\chi^{C(THF)}_{mol,\ dia} = -6 \cdot 10^{-6}$ emu / mol, $\chi^{C(aryl)}_{mol,\ dia} = -6.24 \cdot 10^{-6}$ emu / mol, $\chi^{Li}_{mol,\ dia} = -4.2 \cdot 10^{-6}$ emu / mol, $\chi^{Si}_{mol,\ dia} = -1.5 \cdot 10^{-6}$ emu / mol, $\chi^{Cl}_{mol,\ dia} = -2.6 \cdot 10^{-5}$ emu / mol, $\chi^{Mn(III)}_{mol,\ dia} = -1.1 \cdot 10^{-5}$ emu / mol, $\chi^{Mn(II)}_{mol,\ dia} = -1.4 \cdot 10^{-5}$ emu / mol.

1 H. Landolt, R. Börnstein, O. Madelung, *Numerical data and functional relationships in science and technology: new series - Macroscopic and technical properties of matter*, Springer, Berlin, 1974.

Results:

Sample: $Mn^{II}Li_4Cl_2[(Ph_2SiO)_2O]_2(THF)_5$

χ_{mol}= 0.0168 emu / mol

$\chi_{mol,\ dia}$= $-5.59 \cdot 10^{-4}$ emu / mol

$\chi_{mol,\ corr}$ = 0.0174 emu / mol

μ/μ_B = 6.40

Sample: $Mn^{III}Li_2Cl[(Ph_2SiO)_2O]_2(THF)_4$ (3)

χ_{mol}= 0.0105 emu / mol

$\chi_{mol,\ dia}$= $-4.89 \cdot 10^{-4}$ emu / mol

$\chi_{mol,\ corr}$ = 0.0110 emu / mol

μ/μ_B = 5.10

3. EPR measurements

Sample preparation/ Instrumental details

For the EPR measurements, solution samples of 5 mM concentration in dry THF (99.5% from Acros organics) were prepared. Sample preparation was carried out in a Schlenk-glovebox under nitrogen atmosphere with less than 0.1ppm of oxygen and water.

Q-band CW EPR (33.9 GHz) measurements were conducted on a Bruker EMX-plus spectrometer, using an ER5106QT resonator with conventional perpendicular polarization mode. Microwave power was adjusted on 10mW. Modulation amplitudes of 0.5mT were used during measurements. Modulation frequency was set to 100 kHz. A closed cycle cryostat (ARS4WH, www.arscryo.com) was used for cooling down to 20 K and 7 K. At higher temperatures, no spectra could be obtained. Spectral simulations were performed in Matlab using the EasySpin software package [1].

Results and discussion

(A) Mn(II)-spectrum

The Mn(II) complex, compound **2**, is of the kind of five-coordinated manganese with just one chloride ligand (general form of [MnL_5X]) which is considered among the rare cases, since most of the Mn(II) complexes are found in form of dihalide compounds [2]. The EPR spectrum of the Mn(II) complex shows the characteristic hyperfine resonance lines of a d^5 high spin system, although the outermost high field lines were outside the magnetic field range of the spectrometer and could not be fully observed (Fig. S2). The spectrum looks very different from those of the common Mn(II) complexes, revealing a strong g-anisotropy spreading from g = 10 to g = 1.8. Similar observations were reported for another monochloride five-coordinated Mn(II) complex [3]. Such a high g-anisotropy could be in part due to the contribution of the spin-orbit coupling of the halide, as well as the low symmetry of the overall structure of the complex [2,4].

The major spectral features could be well simulated using $|D| = 0.164\text{cm}^{-1}$ and E/D value of 0.27 which reflects the highly orthorhombic character of this complex [5]. This lowering of the symmetry could be observed as well from the provided crystal structure which predicts a nearly square planar symmetry around manganese nuclei.

The ^{55}Mn hyperfine coupling was found to be about 450 MHz at g_{eff} = 2.64, indicating highly localized spin density on the manganese nuclei. The -2D ($|-\frac{1}{2}\rangle\rightarrow|-\frac{3}{2}\rangle$ and $|+\frac{3}{2}\rangle\rightarrow|+\frac{1}{2}\rangle$ transitions) and -4D ($|+\frac{5}{2}\rangle\rightarrow|+\frac{3}{2}\rangle$ and $|-\frac{3}{2}\rangle\rightarrow|-\frac{5}{2}\rangle$) transitions could be estimated at 900mT and 590mT field positions, similar to field positions reported before [6]. The experimental and corresponding simulated spectra are given in Figure S2.

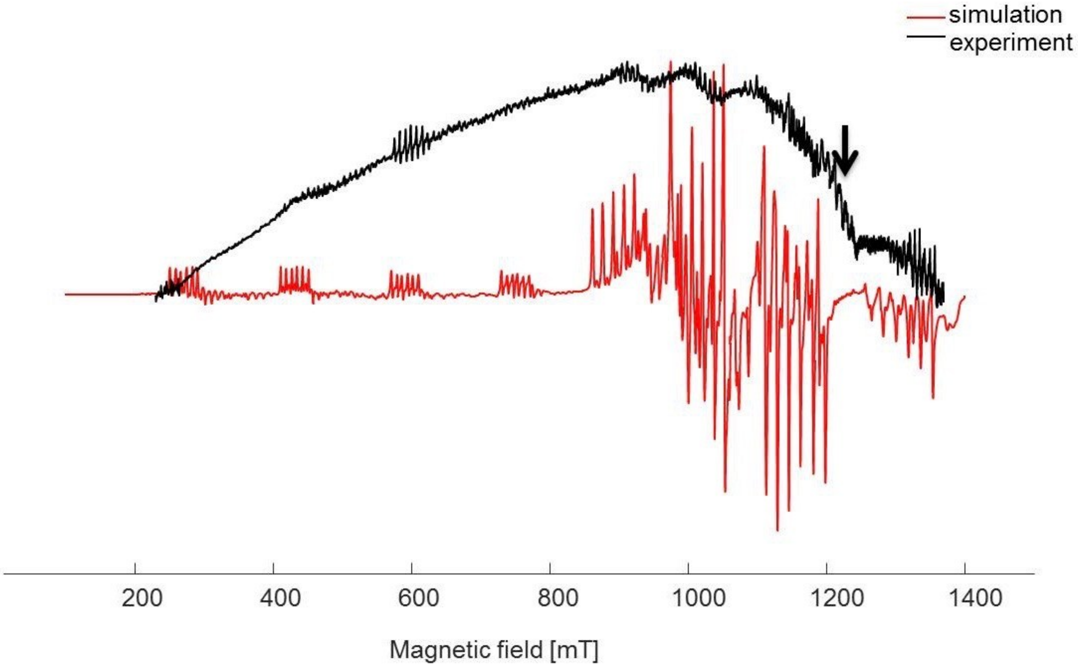

Fig. S2. Experimental CW EPR spectrum of the Mn(II) complex **2** in THF (in black) and its simulation (in red) at 34 GHz using a_{iso}(55Mn) = 16 mZ, g = [1.79 2.04 4.12], IDI = 0.164 cm^{-1}, E/D = 0.27. The arrow at g = 2.06 shows the signal originating from the resonator itself.

(B) Mn(III)-spectrum

The non-Kramers spin state S = 2 of the Mn(III) could be considered as “EPR –silent”, due to either very large zero field splittings (zfs) parameter ($0.6 \leq D \leq 49.9$ cm^{-1}) or fast spin relaxation [7-9]. Since in most cases zfs splittings are larger than the normally available microwave quantum (0.3 and 1.2 cm^{-1} for X- and Q-band, respectively) therefore, identifying Mn(III) with conventional EPR spectroscopy in perpendicular mode setup is rather difficult at these frequencies.

The recorded CW EPR Q-band spectra of the Mn(III) compound **3** in a frozen solution at 7K and 20K (after background correction) are given in Figures S3 and S4. Since the recorded spectra were very broad due to unresolved hyperfine couplings and large zfs parameters, they were analyzed in a qualitative way and were not quantified through simulations.

The signal obtained at 7 K consists of a broad negative, trough-shaped peak with a minimum at an effective g-value (g_{eff}) of 4.5. The feature located at g_{eff} =2.06 arises from the resonator at this temperature. Such trough shape of the signal is already reported for Mn(III) complexes, however at a higher g_{eff} of about 8, using parallel mode at X-band frequencies [10]. The observed transition was related to a $|\pm 2\rangle$ non-Kramers doublet of a high spin Mn(III),d^4, ground state [10,11]. Since herein reported values are related to a completely different complex, this feature could be indicative of a Mn(III) species, which is corroborated by further evidences from magnetic susceptibility measurements. This feature is still observable at higher temperature, however at rather smaller g-value of 3.

Since a Mn (II) impurity in the resonator could also generate such low field features, we have checked for any additional resonances close to g = 2. Comparing to the recorded background spectrum of an empty tube in the resonator, we found no such signal.

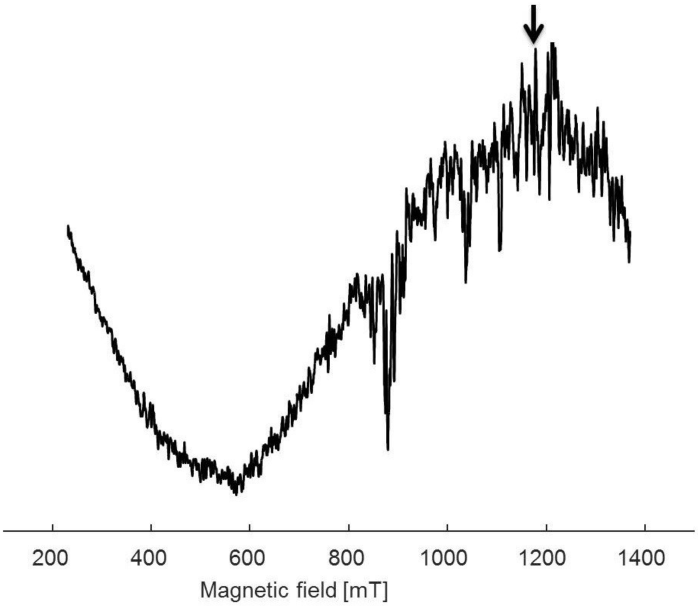

Fig. S3. CW EPR spectrum of the Mn(III) complex **3** in THF at 34 GHz with a g_{eff} of 4.5 at 7 K. The arrow at g = 2.06 shows the signal originating from the resonator itself.

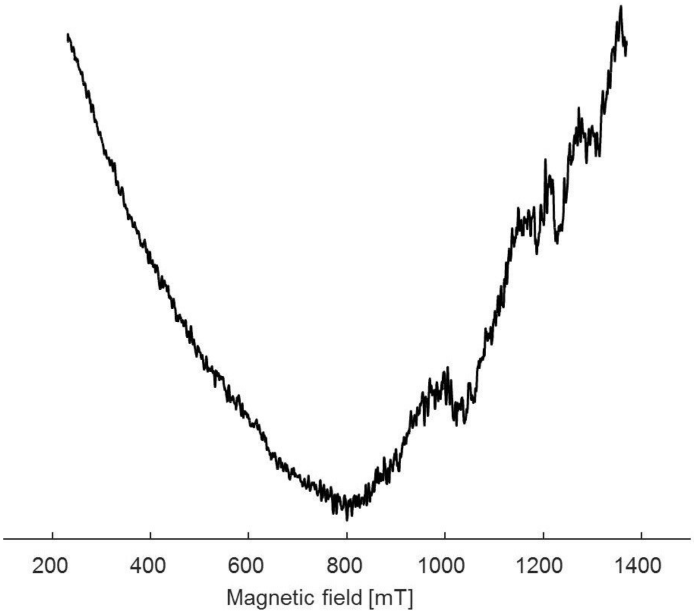

Fig. S4. CW EPR spectrum of the Mn(III) complex **3** in THF at 34 GHz with g_{eff} of 3.0 at 20 K.

References (EPR)

1 S. Stoll, A. Schweiger, *J. Magn. Reson.* 178(1), 42-55 (2006).

2 C. Duboc, M. N. Collomb and F. Neese, Appl Magn Reson 37, 229–245 (2010).

3 C. Bucher, E. Duval, J.M. Barbe, J.N. Verpeaux, C. Amatore, R. Guilard, L. Le Pape, J.M. Latour, S.Dahaoui, C. Lecomte, Inorg. Chem. 40, 5722–5726 (2001).

4 S.R. Chowdhury and S. Mishra,*Phys. Chem. Chem. Phys.* 19, 16914—16922(2017)

5 R.M. Wood, D.M. Stucker, L.M. Jones, W.B. Lynch, S.K. Misra, J.H. Freed, Inorg. Chem. 38, 5384–5388 (1999)

6 D.A.Cleary, A.H.Francis, E.Lifshitz, Chem.Phys.106,123-129 (1986).

7 J.Krzystek , A.Ozarowski, J. Telser. Coord.Chem.Rev. 250. 2308-2324 (2006).

8 S. Mossin, H. Weihe, A.-L. Barra, J. Am. Chem. Soc. 124 ,8764-8765 (2002).

9- A.P. Forshaw, J. M. Smith, A. Ozarowski, J. Krzystek, D. Smirnov, S. A. Zvyagin, T. D. Harris, H. I. Karunadasa, J. M. Zadrozny, A. Schnegg, K.Holldack, T.A. Jackson, A. Alamiri, D.M. Barnes and J.Telser, Inorg. Chem. 52, 144−159 (2013).

10 Y. Sheng, T.A. Stich, K. Barnese, E.B. Gralla, D.Cascio, R. D. Britt, D.E. Cabelli, and J.S.Valentine, J. Am. Chem. Soc. 133, 20878–20889 (2011).

11 S. L. Dexheimer, J. W. Gohdes, M. K. Chan, K.S. Hagen, W. H. Armstrong, and M. P. Klein, J. Am. Chem. Soc,111,24, 8923-8925 (1989).

4. X-Ray crystallographic data for **2** and **3**

STRUCTURE REPORT for 2

Crystallographer: P. Liebing
ID code: li0245
Sample by: Sophie Ehle
Compound: $MnLi_{42}Cl_2\{(Ph_2SiO)_2O\}_2(THF)_5 \cdot 2\ THF$ (**2**)
Formula sum: $C_{76}H_{96}Cl_2Li_4MnO_{13}Si_4$
Formula moieties: $C_{68}H_{80}Cl_2Li_4MnO_{11}Si_4$, 2 C_4H_8O

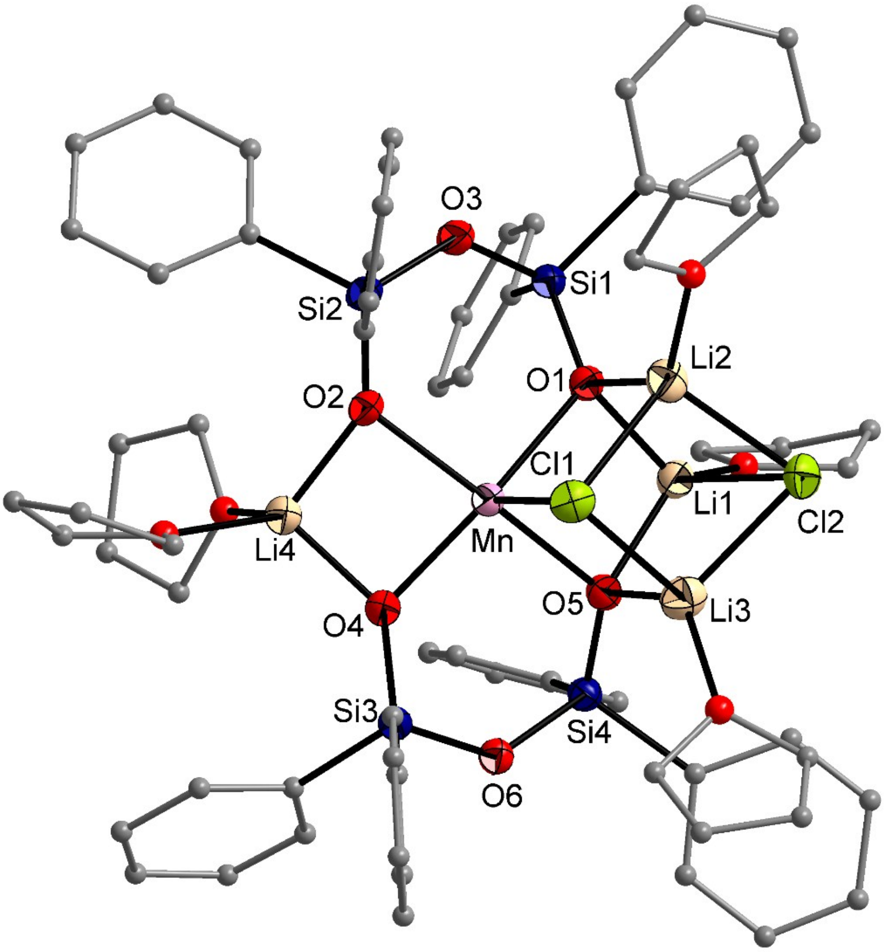

Fig. S5. Molecular structure of the title compound **2** in the crystalline state. Displacement ellipsoids with 40% probability and C atoms as spheres of arbitrary size, H atoms omitted for clarity.

Crystallographic Data and Details on Structure Refinement

formula sum	$C_{76}H_{96}Cl_2Li_4MnO_{13}Si_4$
formula weight	1483.48
crystal color / shape / size (mm)	colorless blocks / 0.32 × 0.25 × 0.25
crystal system	monoclinic
space group	$P2_1/n$
unit cell parameters	
a (Å)	13.5878(3)
b (Å)	42.7842(12)
c (Å)	13.6537(3)
α (deg)	90
β (deg)	98.723(2)
γ (deg)	90
unit cell volume V (Å^3)	7845.7(3)
molecules per cell z	4
crystallographic density ρ_{calcd} (g cm^{-3})	1.256
absorption coefficient μ (mm^{-1})	0.356
diffractometer	STOE IPDS 2T
radiation (λ [Å])	graphite-monochromated Mo-K_α (0.71073)
temperature (°C)	−120
scan type	ω scan (increment 1.5°, exposure 5 min)
completeness of dataset	97.9%
θ range of data collection (deg)	1.904 ... 25.084
reflections collected	40464 ($-16 \leq h \leq 16$, $-50 \leq k \leq 51$, $-16 \leq l \leq 15$)
independent reflections	13659 (R_{int} = 0.0533)
independent reflections with $I>2\sigma(I)$	9458
structure solution method	heavy atom methods (SIR-97)
refinement method	full-matrix least-squares on F^2 (SHELXL 2016/4)
absorption correction method	none
range of transmission factors	–
data / parameters / restraints	13659 / 901 / 170[a]
goodness of fit (GooF) [all data]	1.018
final R values	
R_1 [all data, $I \geq 2\sigma(I)$]	0.0936, 0.0608
wR_2 [all data, $I \geq 2\sigma(I)$]]	0.1712, 0.1551
largest difference peak and hole	0.903 and −0.632 e Å^{-3}
Extinction coefficient	–

Refinement special details: [a] Restraints on interatomic distances and anisotropic displacement parameters (SADI, SIMU) of the THF ligands and non-coordinated THF molecules.

STRUCTURE REPORT for 3

Crystallographer:	F. Engelhardt
ID code:	fe0072
Sample by:	Volker Lorenz
Compound:	**3**
Formula sum:	C72 H88 Cl Li2 Mn O12 Si4
Formula moieties:	C64 H72 Cl Li2 Mn O10 Si4, 2(C4 H8 O)

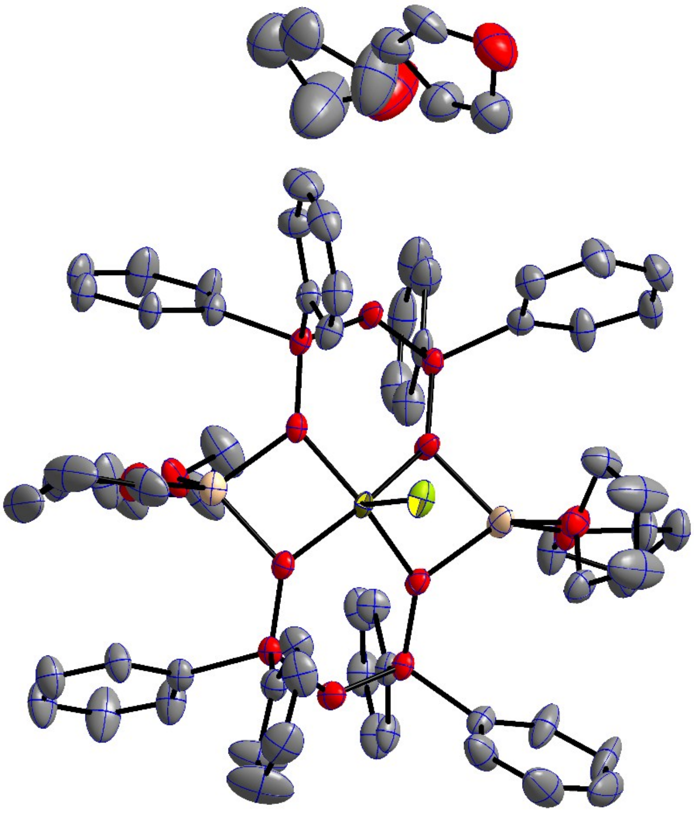

Fig. S6. Molecular structure of the title compound **3** in the crystalline state. Thermal ellipsoids of the heavier atoms with 50% probability, H atoms omitted for clarity.

Crystallographic Data and Details on Structure Refinement

formula sum	C72 H88 Cl Li2 Mn O12 Si4
formula weight	1362.05
crystal size (mm)	0.2 x 0.2 x 0.2 mm
crystal system	Monoclinic
space group	Pn
unit cell parameters	
a (Å)	10.447(3)
b (Å)	15.753(4)
c (Å)	21.429(4)
α (deg)	90
β (deg)	101.33(2)
γ (deg)	90
unit cell volume V (Å^3)	3457.9(15)
molecules per cell z	2
crystallographic density ρ_{calcd} (g cm^{-3})	1.308
absorption coefficient μ (mm^{-1})	0.359

diffractometer	STOE IPDS 2T
radiation (λ [Å])	graphite-monochromated Mo-K$_\alpha$ (0.71073)
temperature (°C)	-173.15
scan type	ω scan (increment 1.5°, exposure 15 min)
completeness of dataset	99.7%
θ range of data collection (deg)	1.938 to 29.430
reflections collected	39936
independent reflections	16641
independent reflections with $I>2\sigma(I)$	
structure solution method	dual-space structure solution (SHELXT)
refinement method	full-matrix least-squares on F^2 (SHELXL 2016/4)
absorption correction method	none
range of transmission factors	-
data / restraints / parameters	16641 / 3816 / 1291
goodness of fit (GooF) [all data]	1.244
final R values	
R_1 [all data, $I \geq 2\sigma(I)$]	0.0714, 0.0660
wR_2 [all data, $I \geq 2\sigma(I)$]]	0.1319, 0.1296
largest difference peak and hole	0.517 and -0.405 eÅ^{-3}

Refinement special details:
Structure shows severe disorder. Solvent as well as coordinating THF molecules are disordered. Additionally, three phenyl moieties show disorder.