Manganese-Calcium Clusters Supported by Calixarenes

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Supporting Information

Complexes of p-t-butylcalix[4]arene, H_4L

Synthesis of $[Mn^{III}_2Mn^{II}_2(OH)_2(L)_2(dmso)_4(EtOH)_2].4EtOH$

The method was adapted from the literature.[1] Calixarene H_4L (100 mg, 0.15 mmol) was slurried in EtOH/DMF (1:1, 20 mL) and dissolved by adding Et_3N (0.1 g, 1.0 mmol). $MnCl_2{\cdot}4H_2O$ (105 mg, 0.53 mmol) and $CaCl_2{\cdot}2H_2O$) (185 mg, 1.26 mmol) were added resulting in a dark purple solution. The resulting solution was filtered and left to evaporate slowly, resulting in the deposition of crystals of $[Mn^{III}_2Mn^{II}_2(OH)_2(L)_2(dmso)_4(EtOH)_2]{\cdot}4EtOH$ suitable for single crystal X-ray structure determination.

$[Mn^{III}_2Mn^{II}_2(OH)_2(L)_2(dmso)_6]{\cdot}6MeOH$ was synthesized by substituting EtOH with MeOH

$[Mn^{III}_2Mn^{II}_2(OH)_2(L)_2(dmso)_4]{\cdot}4dmso{\cdot}4CH_3CN$, and $[Mn^{III}_2Mn^{II}_2(OH)_2(L)_2(dmso)_4]{\cdot}2.5CH_3CN$ were synthesized by substituting EtOH with CH_3CN, with the different solvates being isolated from replicates of the same reaction conditions.

Crystallography

The crystal data for the four $[Mn^{III}_2Mn^{II}_2(OH)_2(L)_2(solvent)_x]$ complexes are summarized in Table S.1. Crystallographic data for the structures were collected at 100(2) K on an Oxford Diffraction Gemini diffractometer fitted with Cu Kα or Mo Kα radiation, as specified. The structures were refined against F^2 with full-matrix least-squares using the program SHELXL-97.[2] Anisotropic displacement parameters were employed for the non-hydrogen atoms, and hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atoms, unless otherwise specified below.

Refinement details:

$[Mn^{III}_2Mn^{II}_2(OH)_2(L)_2(dmso)_4(EtOH)_2].4EtOH$. One ^{t}Bu group, the coordinated ethanol molecule, one of the two dmso molecules and both solvent molecules were all modelled as being disordered over two sets of sites. The occupancies for the two components of the disordered ^{t}Bu group were refined to 0.667(18) and its complement with the site occupancies of the remaining disordered atoms set at 0.5 after trial refinement. Geometries of the atoms of the ^{t}Bu group and solvent EtOH molecules were restrained to ideal values. Hydroxyl hydrogen atoms were not located.

$[Mn^{III}_2Mn^{II}_2(OH)_2(L)_2(dmso)_6]\cdot 6MeOH$. One ^{t}Bu group and the dmso molecule coordinated through the calixarene were both modelled as being disordered over two sets of sites. The occupancy of the ^{t}Bu was refined to 0.567(2) and its complement for the two components. The occupancies of the disordered dmso were constrained to 0.5 after trial refinement. Geometries of the disordered atoms were restrained to ideal values. The site occupancies of two solvent methanol molecules were set at 0.5 after trial refinement, the hydroxyl hydrogen atom of one not being included in the model. The atoms of one of the solvent methanol molecules were refined with isotropic displacement parameters.

$[Mn^{III}_2Mn^{II}_2(OH)_2(L)_2(dmso)_4]\cdot 4dmso\cdot 4CH_3CN$. One ^{t}Bu group, one of the two coordinated dmso molecules and one of the two solvent dmso molecules were all modelled as being disordered over two sets of sites. The occupancies of the disordered ^{t}Bu group and of the coordinated dmso molecule were both refined to 0.568(2) and its complement with those of the solvent dmso molecules refined to 0.685(2) and its complement. Geometries of the atoms of the disordered groups were restrained to ideal values with isotropic refinement of the atoms of the disordered ^{t}Bu group. The hydroxyl hydrogen atom was located and refined with O-H distance restrained to its ideal value. Residual electron density that could not be modelled as solvent was effectively removed by use of the program Squeeze.

$[Mn^{III}_2Mn^{II}_2(OH)_2(L)_2(dmso)_4]\cdot 2.5CH_3CN$. A ^{t}Bu group and one of the two coordinated dmso molecules of molecule 2 were modelled as being disordered over two sets of sites. The occupancies of these disordered atoms and of the atom of the solvent $\mathrm{CH_3CN}$ (9) molecule were set at 0.5 after trial refinement. The methyl carbon atoms of this ^{t}Bu were refined with isotropic displacement parameters. Geometries of the atoms of the disordered $\mathrm{CH_3CN}$ were restrained to ideal values. The O-H distances of the hydroxyl hydrogen atoms in both molecules were also restrained to ideal values.

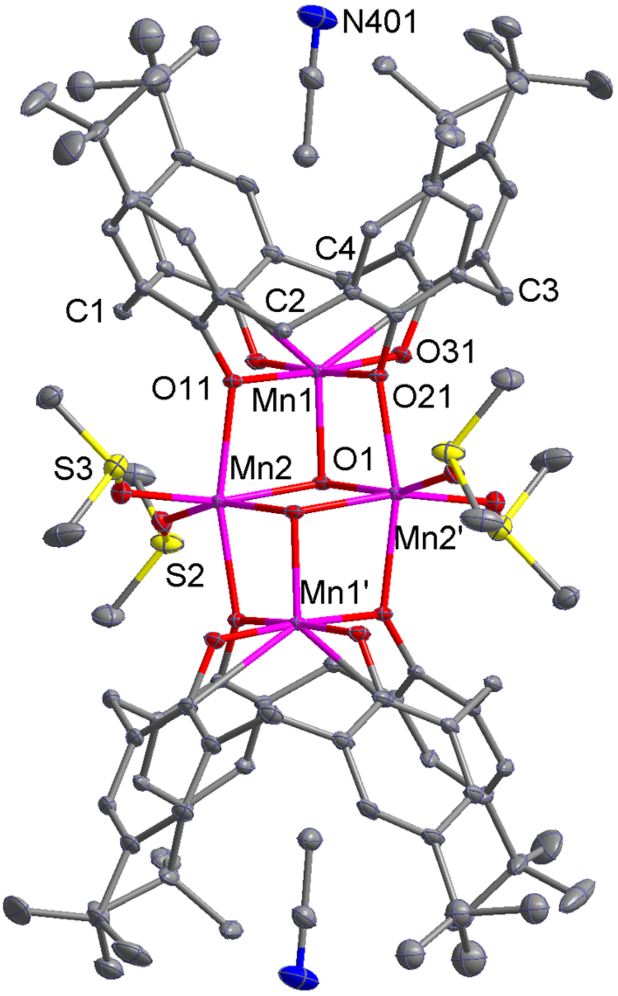


Figure S.1. A representation of a typical example of the $\mathrm{Mn^{III}_2Mn^{II}_2}$ complexes of L, $[\mathrm{Mn^{III}_2Mn^{II}_2(OH)_2(L)_2(dmso)_4}]\cdot 4\mathrm{dmso}\cdot 4\mathrm{CH_3CN}$, showing the complex with included acetonitrile molecules in the calixarene cavities. In this and the following figures, hydrogen atoms have been omitted and ellipsoids have been drawn at the 30% probability level.

Table S.1: Crystal data and refinement details for complexes, *$[Mn^{III}_2Mn^{II}_2(OH)_2(L)_2(solvent)_x]$*. a) $[Mn^{III}_2Mn^{II}_2(OH)_2(L)_2(dmso)_4(EtOH)_2].4EtOH$, b) $[Mn^{III}_2Mn^{II}_2(OH)_2(L)_2(dmso)_6]\cdot 6MeOH$ c) $[Mn^{III}_2Mn^{II}_2(OH)_2(L)_2(dmso)_4]\cdot 4dmso\cdot 4CH_3CN$, d) $[Mn^{III}_2Mn^{II}_2(OH)_2(L)_2(dmso)_4]\cdot 2.5CH_3CN$

	a)	b)	c)	d)
Empirical formula	$C_{108}H_{166}Mn_4O_{20}S_4$	$C_{106}H_{166}Mn_4O_{22}S_6$	$C_{112}H_{166}Mn_4N_4O_{18}S_8$	$C_{101}H_{137.50}Mn_4N_{2.50}O_{14}S_4$
Formula weight	2132.41	2204.51	2332.73	1958.61
Temperature	100(2) K	100(2) K	100(2) K	100(2) K
Wavelength	1.54178 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.1507(16)	12.6063(5)	11.9244(3)	11.7551(4)
b (Å)	12.4163(16)	12.8277(4)	13.7635(4)	20.5583(7)
c (Å)	18.597(2)	19.4569(7)	20.6536(6)	21.0755(7)
α (°)	87.084(10)	107.436(3)	77.570(2)	88.406(3)
β (°)	83.453(10)	107.941(3)	74.825(2)	86.173(3)
γ (°)	84.328(11)	91.075(3)	76.351(2)	86.900(3)
Volume (Å^3)	2771.4(6)	2834.38(18)	3136.26(15)	5072.9(3)
Z	1	1	1	2
ρ_{calc} (Mg m^{-3})	1.278	1.292	1.235	1.282
μ (mm^{-1})	4.841	0.611	0.586	0.628
Crystal size (mm^3)	0.17 x 0.10 x 0.05	0.50 x 0.26 x 0.07	0.84 x 0.45 x 0.08	0.52 x 0.06 x 0.02
θ range (°)	3.58 to 68.59	3.62 to 30.80	3.49 to 36.48	3.48 to 29.22
Index ranges	-14<=h<=14, -14<=k<=14, -19<=l<=21	-17<=h<=17, -18<=k<=18, -27<=l<=16	-19<=h<=19, -22<=k<=22, -34<=l<=34	-15<=h<=15, -26<=k<=26, -22<=l<=28
Reflections collected	27053	27951	93796	55451
Independent reflections (R_{int})	9837 (0.1295)	15454 (0.0452)	29089 (0.0438)	23826 (0.0709)
Completeness	98.2 % to θ= 67.50°	98.7 % to θ = 28.75°	99.8 % to θ = 30.00°	98.6 % to θ = 27.00°
Absorption correction	Analytical	Analytical	Analytical	Semi-empirical from equivalents
Transmission (min, max)	0.509 and 0.797	0.812 and 0.964	0.774 and 0.960	0.98/1.00
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	9837 / 51 / 642	15454 / 57 / 688	29089 / 27 / 732	23826 / 41 / 1200
Goodness-of-fit on F^2	0.875	0.960	1.011	0.784
Final R indices [I>2σ(I)]	R_1 = 0.0903, wR_2 = 0.2195	R_1 = 0.0656, wR_2 = 0.1705	R_1 = 0.0679, wR_2 = 0.1908	R_1 = 0.0508, wR_2 = 0.0841
R indices (all data)	R_1 = 0.1898, wR_2 = 0.2614	R_1 = 0.1131, wR_2 = 0.1847	R_1 = 0.1132, wR_2 = 0.2055	R_1 = 0.1315, wR_2 = 0.0939
Largest diff. peak and hole	0.848 and -0.711 e.Å^{-3}	1.818 and -1.712 e.Å^{-3}	2.013 and -1.871 e.Å^{-3}	1.254 and -0.604 e.Å^{-3}
CCDC No.	983277	983278	983279	983280

Complexes of p-t-butylsulfonylcalix[4]arene, H_4L^{SO2}

$HNEt_3[Mn_4(OH)(L^{SO2})_2]$

Synthesis: $H_4L^{SO}\cdot CHCl_3$ (90 mg, 0.10 mmol) was suspended in a solution of MeOH/$CHCl_3$ (15 ml/15 mL). To this was added $MnCl_2.4H_2O$ (20 mg, 0.10 mmol) and $CaCl_2.2H_2O$ (16 mg, 0.11 mmol). Following stirring overnight, 3 drops of Et_3N were added, resulting in a colour change from colourless to light pink over 4 hours. Cube-like light yellow crystals were deposited after 14 days. These were subject to a single crystal X-ray structure determination, which gave results consistent with a formulation $HNEt_3[Mn_4(OH)(L^{SO2})_2]\cdot 3.33CHCl_3\cdot MeOH$. The crystals were isolated and dried under ambient conditions (99 mg, 79.3 %). Analysis: $(C_{40}H_{44}O_{12}S_4)_2Mn_4OH.(Et_3NH).(CHCl_3)$ calc. C: 48.64, H: 4.97, N: 0.65, found C: 48.44, H: 4.88, N: 0.91. The procedure was repeated, resulting in crystals of a different solvate $HNEt_3[Mn_4(OH)(L^{SO2})_2]\cdot 2CHCl_3\cdot MeOH$, as determined by a structural analysis.

Crystallography:

The crystal data for $HNEt_3[Mn_4(OH)(L^{SO2})_2]\cdot 3.33CHCl_3\cdot MeOH$ are summarized in Table S.2. Diffraction data were collected at 100(2) K on an Oxford Diffraction Gemini diffractometer fitted with graphite-monochromated Mo Kα radiation. Following analytical absorption corrections and solution by direct methods, the structure was refined against F^2 with full-matrix least-squares using the program SHELXL-97.[2] One complete phenyl group, 1n, was modelled as being disordered over two sets of sites with occupancies refined to 0.667(5) and its complement. The site occupancy of the solvent $CHCl_3$ in the cavity was constrained to be the same after trial refinement showed it to be not significantly different. The solvent in both cavities were modelled as being disordered about the crystallographic 2 axis. The cation was modelled as one triethylammonium ion hydrogen bonded to a molecule of methanol, both of which were disordered about a crystallographic 2-fold and were therefore refined with occupancies of 0.5. Geometries and ADP's of the disordered atoms were restrained to reasonable values. The central atom was modelled as an oxo group. Attempts to model this as a hydroxyl group, disordered over two sites were very unsatisfactory. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen on the methanol OH was not located. All remaining hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atoms.

The crystal data for $HNEt_3[Mn_4(OH)(L^{SO2})_2]\cdot 2.66CHCl_3\cdot MeOH$ are summarized in Table S.2. . Diffraction data were collected at 150(2) K on an Oxford Diffraction Gemini diffractometer fitted with a Cu Kα radiation source. Following analytical absorption corrections and solution by direct methods, the structure was refined against F^2 with full-matrix least-squares using the program SHELXL-97.[2] The cation was modelled as being $HNEt_3^+$ disordered about a crystallographic inversion centre. The solvent molecule in the calix was modelled as being part MeOH and part $CHCl_3$ with the site occupancy of the former constrained to 0.5 after trial refinement with that of the latter refined to 0.33(1). As a result of this disorder, one ^{t}BuPhO moiety was also found to be disordered over two sites, and was refined with site occupancies constrained to 0.5. Geometries of the cation and solvent molecules were restrained to ideal values. Solvent hydroxyl hydrogen atom was not located. All remaining hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters.

$[L^{SO2}\cdot(Mn\cdot 2dmf\cdot H_2O)_2]\cdot 4dmf$

Synthesis: $H_4L^{SO2}\cdot CHCl_3$ (99 mg, 0.10 mmol) was dissolved in dmf (1 mL), after which was added 6 drops of Et_3N, and the solution swirled. To this was added a solution of $MnCl_2.4H_2O$ (20 mg, 0.10 mmol) and $CaCl_2.2H_2O$ (16 mg, 0.11 mmol) in dmf (1 mL). A pale ppt formed uniformly throughout the solution, and was collected (86 mg). Small yellow crystals formed in the mother liquor over a period of 60 days (1.4 mg, 0.9%). Single crystal x-ray structure determination confirmed that the product was $[L^{SO2}\cdot(Mn\cdot 2dmf\cdot H_2O)_2]\cdot 4dmf$.

Alternate synthesis: To a stirring suspension of $H_4L^{SO2}\cdot CHCl_3$ (101 mg, 0.11 mmol) in $CHCl_3$/MeOH (2.5 mL/ 2.5 mL), was added $Mn(OAc)_2\cdot 4H_2O$ (26 mg, 0.11 mmol) and $Ca(OAc)_2\cdot H_2O$ (18 mg, 0.10 mmol). After 2 hours, the reaction mixture was evaporated to dryness. This was dissolved in 10 mL of dmf, to which was added NH_4Cl (3.3 mg, 0.06 mmol) in EtOH (2 mL). After 60 days, large yellow crystals were isolated (45 mg, 27.6%). Single crystal x-ray structure determination confirmed that the product was again $[L^{SO2}\cdot(Mn\cdot 2dmf\cdot H_2O)_2]\cdot 4dmf$, with this structure being the better quality of the two, and hence is the one reported here.

Crystallography: The crystal data for $[L^{SO2}.(Mn.2dmf.H_2O)_2].4dmf$ are summarized in Table S.2. Diffraction data were collected at 100(2) K on an Oxford Diffraction Xcalibur diffractometer fitted with Mo Kα radiation. Following analytical absorption corrections and solution by direct methods, the structure was refined against F^2 with full-matrix least-squares using the program SHELXL-97.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. The water molecule hydrogen atoms were located and refined with O-H distances restrained to ideal values. All remaining hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atoms.

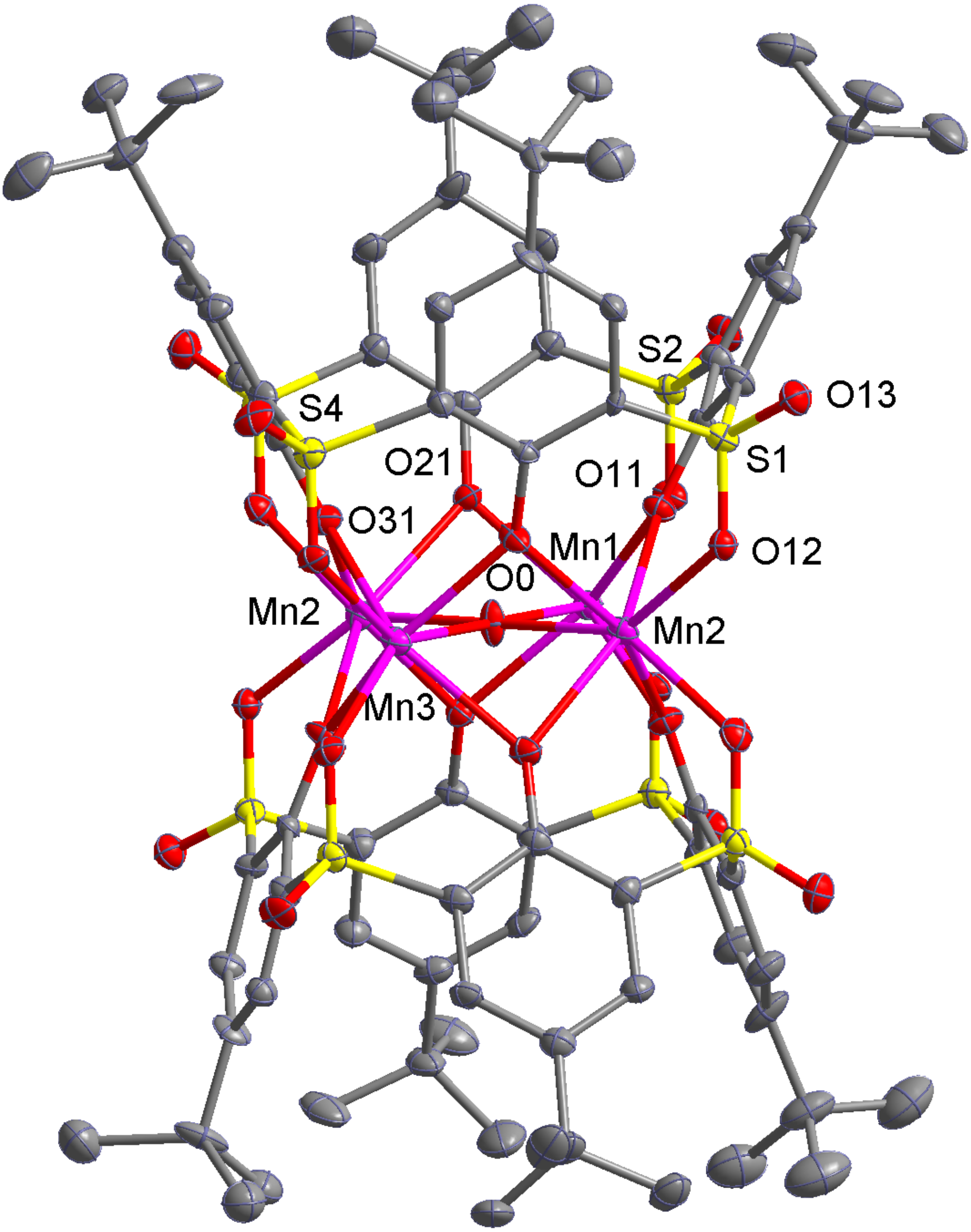


Figure S.2. The complex anion from $HNEt_3[Mn_4(OH)(L^{SO2})_2]\cdot 2.66CHCl_3\cdot MeOH$

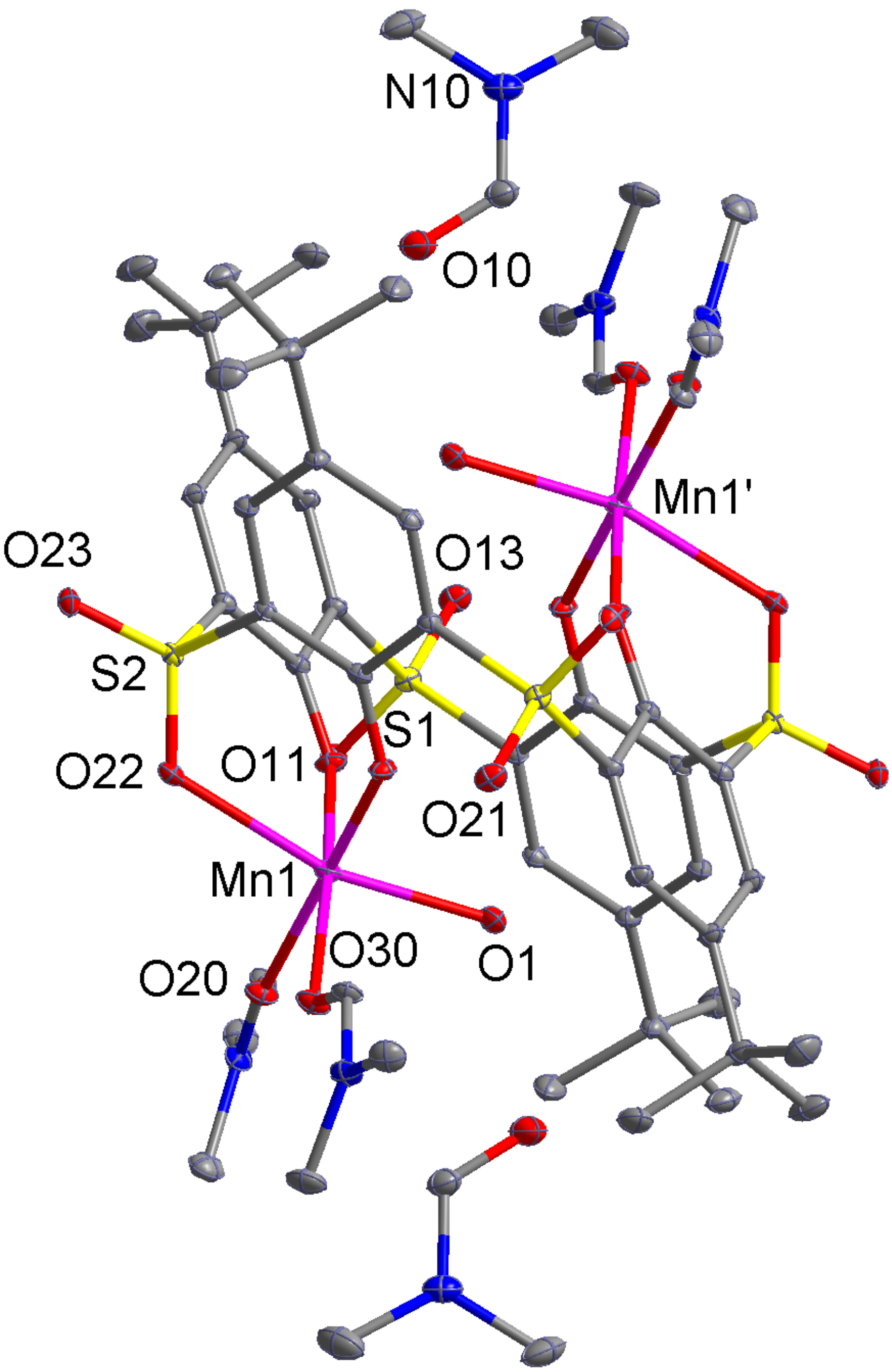


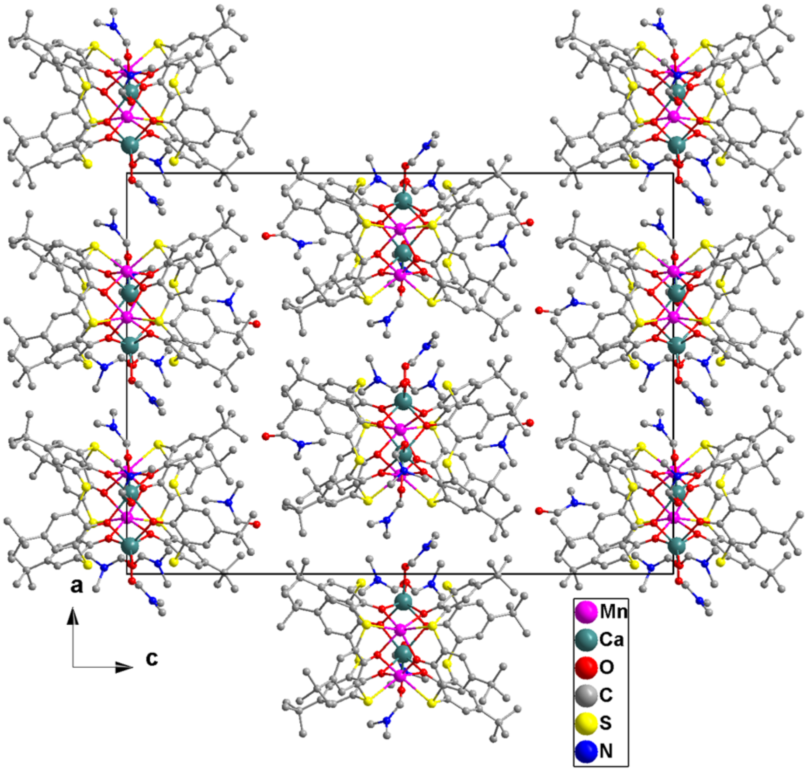
Figure S.3. The complex found in [L^{SO2}.(Mn.2dmf.H$_2$O)$_2$].4dmf

Table S.2: Crystal data and refinement details for a) $HNEt_3[Mn_4(OH)(L^{SO2})_2]\cdot 3.33CHCl_3\cdot MeOH$, b) $HNEt_3[Mn_4(OH)(L^{SO2})_2]\cdot 2.66CHCl_3\cdot MeOH$ and c) $[L^{SO2}.(Mn.2dmf.H_2O)_2].4dmf$.

Complex	a	b	c
Empirical Formula	$C_{90.33}H_{111.33}Cl_{10}Mn_4NO_{26}S_8$	$C_{89.60}H_{110.65}Cl_{7.96}Mn_4NO_{26}S_8$	$C_{64}H_{104}Mn_2N_8O_{22}S_4$
Formula Weight (g/mol)	2457.83	2376.06	1575.67
Temperature (K)	100(2)	150(2)	100(2)
Wavelength (Å)	0.71073	1.54178	0.71073
Radiation	Mo Kα	Cu Kα	Mo Kα
Crystal System	Monoclinic	Monoclinic	Triclinic
Space Group	*C*2/c	*C*2/c	P**Error!**
a (Å)	22.8348(6)	19.1478(11)	12.2456(2)
b (Å)	19.0750(4)	22.9180(9)	12.2526(2)
c (Å)	25.8552(8)	24.6864(14)	13.5403(3)
α (°)	90	90	78.279(2)
β (°)	109.298(3)	98.617(5)	81.427(2)
γ (°)	90	90	84.009(1)
Volume ($Å^3$)	10629.1(5)	10710.8(10)	1961.24(6)
Z	4	4	1
ρ ($Mg\ m^{-3}$)	1.536	1.473	1.334
μ (mm^{-1})	0.944	7.620	0.502
Crystal size (mm^3)	0.19 × 0.16 × 0.06	0.19 × 0.11 × 0.08	0.64 × 0.41 × 0.27
θ range (°)	3.59 to 34.66	3.03 to 67.30	3.07 to 37.16
Index ranges	-35<=h<=33, -30<=k<=29, -40<=l<=39	-21<=h<=22, -27<=k<=21, -29<=l<=29	-20<=h<=20, -20<=k<=20, -22<=l<=22
Reflections Collected	70113	47679	72083
Independent reflections (R_{int})	21581 (0.0518)	9516 (0.0820)	19514 (0.0338)
Completeness	99.5 % to θ = 33.50°	99.1 % to θ = 67.30°	99.6 % to θ = 30.00°
Absorption correction	Analytical	Analytical	Analytical
Transmission (min, max)	0.876, 0.953	0.489, 0.666	0.822, 0.901
Data/restraints/parameters	21581/136/701	9516/274/766	19514/2/472
Goodness-of-fit on F^2	1.013	1.487	0.987
Final *R* indices [$I>2\sigma(I)$]	R_1=0.0657, wR_2=0.1863	R_1=0.1150, wR_2=0.3614	R_1=0.0647, wR_2=0.1797
R indices (all data)	R_1=0.1174, wR_2=0.1996	R_1=0.1310, wR_2=0.3726	R_1=0.0795, wR_2=0.1855
Largest diff. peak and hole	1.780 and -1.789 e.$Å^{-3}$	2.199 and -0.902 e.$Å^{-3}$	2.810 and -0.551 e.$Å^{-3}$
CCDC No.	983282	983285	983287

Unit Cell Diagrams of 1 and 2

(a)



(b)

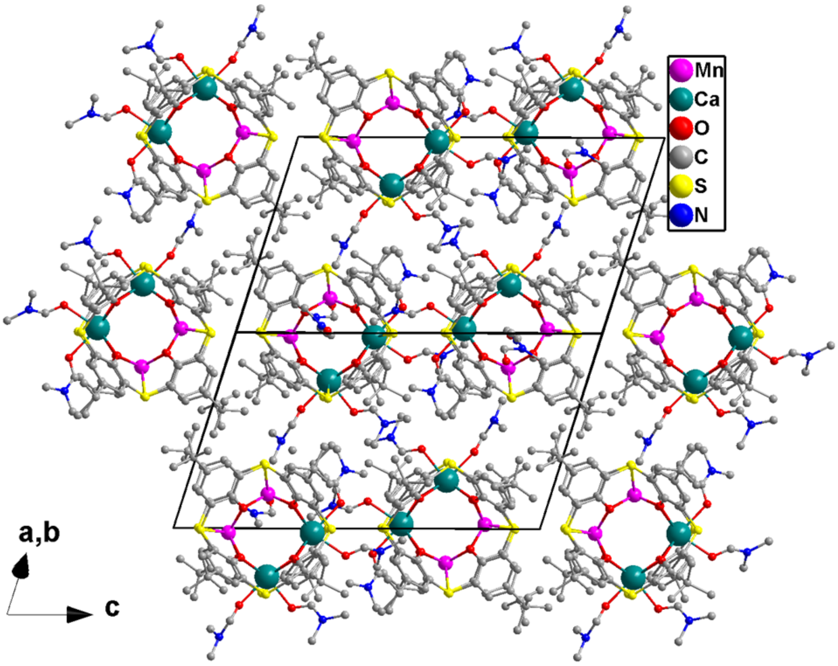


Figure S.4. Solvates of [$Mn_2(Ca\cdot 2dmf)_2(L^S)_2$], **1**. (a) The unit cell content of **1**$\cdot$3dmf$\cdot$0.4H_2O projected down the *b*-axis (b) The unit cell content of **1**$\cdot$2dmf projected along the *ab* diagonal.

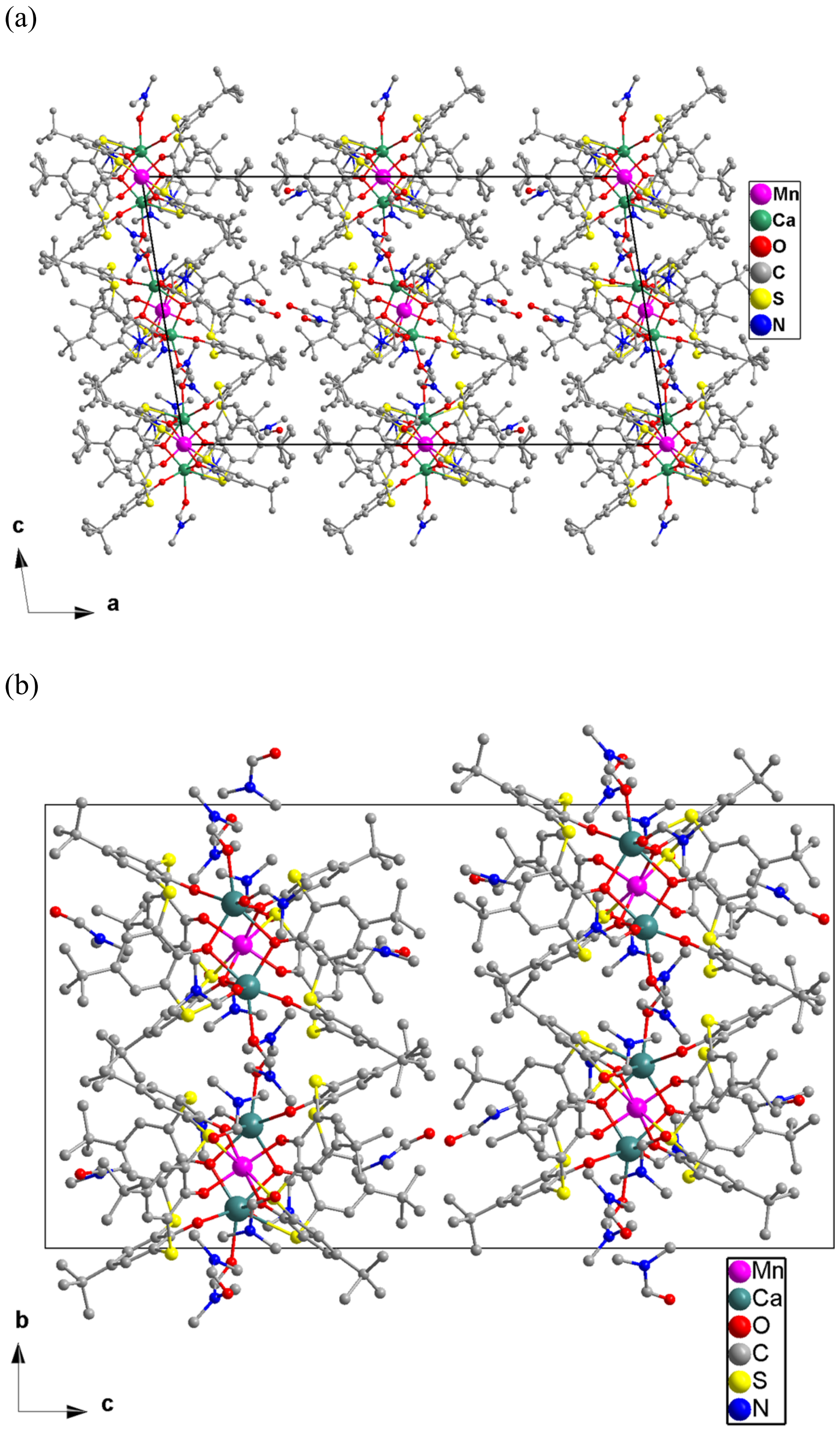


Figure S.5. Solvates of [Mn(Ca·2DMF)$_2$(HL^S)$_2$], **2**. (a) The unit cell content of **2**·4dmf projected down the *b*-axis (b) The unit cell content of **2**·3.55dmf projected along the *a*-axis.

1. Karotsis, G.; Teat, S. J.; Wernsdorfer, W.; Piligkos, S.; Dalgarno, S. J.; Brechin, E. K., *Angew. Chem., Int. Ed.* **2009,** *48*, 8285-8288, S8285/1-S8285/4.
2. Sheldrick, G. M., *Acta Crystallogr. A* **2008,** *64*, 112-122.