Electronic Supplementary Information

Exchange-coupled oxygen- and sulfur-bridged cyclopentadienyl-manganese(II) cages

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Synthetic details

General considerations. Toluene was dried by refluxing under nitrogen for several hours over sodium-potassium alloy. Benzene-*d*$_6$ was distilled from sodium-potassium alloy and stored over activated 4 Å molecular sieves. Solids were manipulated using an MBraun LabMaster glovebox under an argon atmosphere, and solutions were transferred using a Schlenk line under nitrogen that had been passed through several columns of various drying agents and a heated copper catalyst. Manganocene, Cp_2Mn[1] and lithium triphenthylsilylthiolate[2] were synthesized according to literature procedures, and triphenylsilanol was purchased from Aldrich and used as supplied. Paramagnetic ^{1}H NMR spectra were acquired using a Bruker Avance III 400 MHz spectrometer across a chemical shift range of 250 ppm. Elemental analysis results were obtained using the elemental analysis service of London Metropolitan University, U.K. (Mr. S. Boyer).

Compound 1: deprotonation route. A solution of Cp_2Mn (0.10 g, 0.55 mmol) in toluene (10 ml) was added to a stirred suspension of Ph_3SiOH (0.15 g, 0.55 mmol) at –78 C. The light green reaction mixture was warmed to room temperature and stirred overnight. The resulting amber solution was briefly heated to dissolve a pale yellow precipitate and then filtered (porosity 3). The volume of the filtrate was reduced until appreciable amounts of precipitate had formed on the walls of the reaction vessel, and then the mixture was gently heated until a homogeneous solution was obtained. Storage at room temperature produced a crop of large, colourless block-like crystals, which were subsequently identified by X-ray crystallography to be **1**·(1.5 toluene). Placing the crystals under vacuum for 30 minutes resulted in the formation of toluene-free **1** (isolated yield 0.14 g, 55% based on manganese). Analysis calculated for $C_{82}H_{70}O_4Si_4Mn_3$: C 70.52, H 5.05; found C 70.59, H 5.65. ^{1}H NMR (benzene-*d*$_6$, 400.13 MHz, 298 K, /ppm): 2.04, 1.18, 0.80, 2, 1 and 2 ^{1}H, respectively, phenyl. Cp protons not observed.

Compound **2** can be synthesized using this method, on the same scale, with typical yields of 40-45%.

Compound 2: transmetallation route. A solution of Cp_2Mn (0.10 g, 0.55 mmol) in toluene (10 ml) was added to a stirred suspension of Ph_3SiSLi (0.16 g, 0.55 mmol) in toluene (10 ml) at –78 C. The yellow reaction mixture was warmed to room temperature and stirred overnight, and then filtered (porosity 3) to remove a gelatinous precipitate of CpLi. The solvent was evaporated and the resulting yellow solid then washed with pentane (2 mL) and then dried. Toluene (5 mL) was and the dark yellow mixture was gently heated until a homogeneous solution was obtained. Storage at –28 C produced a crop of yellow crystals, which were subsequently identified by X-ray crystallography to be **2**·(3.5 toluene)·(1 toluene). Placing the crystals under vacuum for 60 minutes resulted in the formation of toluene-free **2** (isolated yield 0.12 g, 53% based on manganese). Analysis calculated for $C_{92}H_{80}S_4Si_4Mn_4$: C 67.13, H 4.90; found C 67.87, H 4.21. ^{1}H NMR (benzene-*d*$_6$, 400.13 MHz, 298 K, /ppm): 2.91, 2.62, 2.02, 2, 1 and 2 ^{1}H, respectively, phenyl. Cp protons not observed.

Compound **1** can be synthesized using this method, on the same scale, with typical yields of 55-60%.

X-ray crystallography

Data on **1**·(1.5 toluene) were collected using a Bruker APEX CCD diffractometer, and data on **2**·(3 toluene)·(*n*-pentane) were collected using an Agilent Technologies SuperNova CCD diffractometer. For **2**·(3 toluene)·(*n*-pentane), a multi-scan absorption correction was applied to the data.[3] The structures were solved with SHELXS, and SHELXL was used for the refinement.[4]

In **1**·(1.5 toluene), the asymmetric unit contains one molecule of **1** and 1.5 toluene solvent molecules, with the toluene at half occupancy disordered over a centre of symmetry. All non-H atoms were refined anisotropically with restraints on the adps of some of the carbon atoms, except the toluene at half-occupancy, which was refined isotropically with a common adp. All the phenyl groups were constrained to be regular hexagons and restraints were applied to the Ph–Me single bond lengths. The Cp rings were constrained to be regular pentagons. H-atoms were included in calculated positions. The crystals diffracted extremely weakly, which led to a high R_{int} value and a low percentage of data with $I > 2\ (I)$. It was also necessary to cut the data at 0.9 Å resolution because there was no diffraction beyond this point.

The crystal structure of **2** contains three toluene molecules and one *n*-pentane one which is located at the three-fold rotary-inversion axis. The disordered toluene molecule could be modelled with isotropic minor position. The *n*-pentane solvent was treated with the SQUEEZE function of the PLATON software.[5] The void contains 41 electrons (42 electrons for pentane) in a cavity of 188 Å^3.

Table S1. Crystal data and structure refinement for **1**·(1.5 toluene) and **2**·(3 toluene)·(pentane)[a]

	1·(1.5 toluene)	**2·(3 toluene)·(pentane)**
Empirical formula	$C_{92.5}H_{82}Mn_3O_4Si_4$	$C_{119}H_{117}Mn_4S_4Si_4$
Formula weight	1534.76	1935.38
T/K	100(2)	123(1)
/Å	0.71073	1.54178
Crystal system	monoclinic	trigonal
Space group	*P*2$_1$/*n*	*P*3
a/Å	14.632(4)	20.0897(2)
b/Å	26.084(8)	20.0897(2)
c/Å	20.375(6)	14.0486(2)
/°	90	90
/°	94.221(6)	90
/°	90	120
V/Å^3	7755(4)	4910.33(14)
Z	4	2
Density (calculated)/Mg m^{-3}	1.315	1.339
Crystal size/mm^3	0.45 0.17 0.11	0.42 0.28 0.24
range for data collection/°	2.09-23.26	3.15-74.20
Reflections collected	46182	24724
Independent reflections	11108 [*R*(int) = 0.3053]	6497 [R_{int} = 0.0351]
Completeness/%	99.7 %	97.3 %
Data / restraints / parameters	11108 / 681 / 740	6497 / 0 / 408
Goodness-of-fit on F^2	0.734	1.033
Final *R* indices [I>2 (I)]	$R_1 = 0.0777$, $wR_2 = 0.1479$	$R_1 = 0.0402$, $wR_2 = 0.1094$
R indices (all data)	$R_1 = 0.2669$, $wR_2 = 0.1899$	$R_1 = 0.0423$, $wR_2 = 0.1106$
Largest diff. peak and hole/e.Å^{-3}	0.785 and -0.477	0.796 and -0.558

[a] Full-matrix least-squares on F^2 used as structure refinement for both compounds.

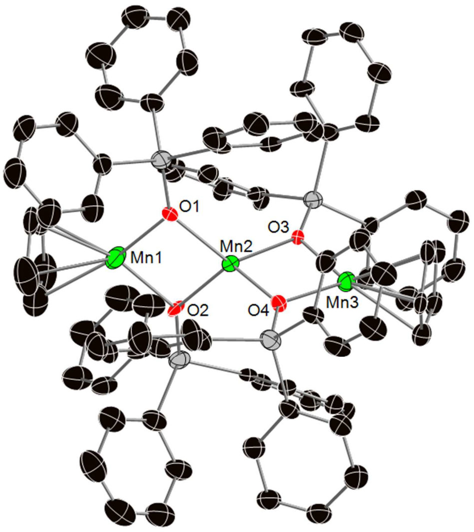

Figure S1. Thermal ellipsoid plots (50% probability) of the molecular structures of **1**. Unlabelled atoms are carbon (black) and silicon (grey). Hydrogen atoms not shown.

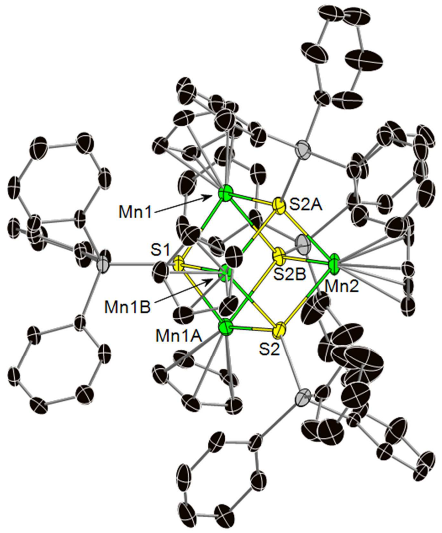

Figure S2. Thermal ellipsoid plots (50% probability) of the molecular structure of **2**, viewed along the crystallographic *b*-axis. Unlabelled atoms are carbon (black) and silicon (grey). The "A"and "B" atom labels indicates that these atoms are at equivalent positions. Hydrogen atoms are not shown.

Magnetic susceptibility measurements on 1 and 2

The magnetic properties of polycrystalline samples of **1** and **2** were measured using a Quantum Design MPMS-7 SQUID magnetometer at temperatures in the range 2-300 K. In a glove box, the polycrystalline samples were transferred to Kel-F capsules, which were then sealed with an O-ring cap, and the capsules were then placed in plastic straws. One end of the straw was then sealed with a cap, and the other end was sealed with Blu-Tac. The straw was then sealed in a Schlenk tube and taken to the magnetometer. The straw was removed from the Schlenk tube and the Blu-Tac quickly replaced with the carbon fibre rod, and then the sample was quickly transferred to the purged sample space of the MPMS.

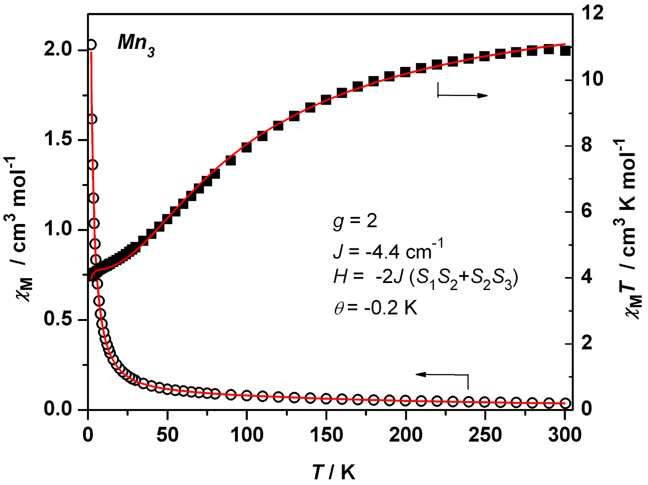

Figure S3. Temperature dependence of χ_M (squares) and $\chi_M T$ (circles) of **1**.

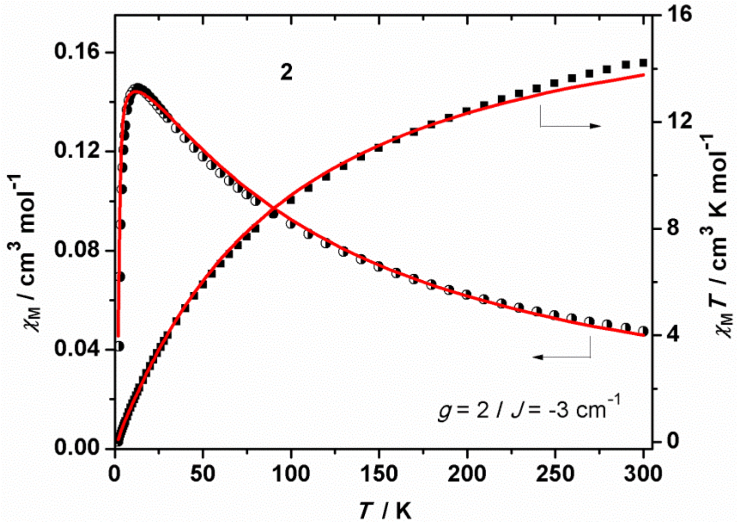

Figure S4. Temperature dependence of χ_M (squares) and $\chi_M T$ (circles) of **2**.

References

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