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Supplementary Material

Heterometallic tetranuclear $\{Mn^{III}_2Ln^{III}_2\}_n$ 1-D coordination polymers: Employing sulfonate ligands as connecting groups

Stuart K. Langley,[a] Boujemaa Moubaraki[a] and Keith S. Murray[a*]

[a] ***School of Chemistry, Monash University, Clayton, Victoria 3800, Australia***

***email: keith.murray@monash.edu**

Table S1. Crystallographic data for compounds **1 - 5**.

	1	**2**	**3**	**4**
Formula[A]	$Mn_2Pr_2C_{42}H_{51}O_{26}N_9S_2$	$Mn_2Nd_2C_{42}H_{51}O_{26}N_9S_2$	$Mn_2Gd_2C_{42}H_{51}O_{26}N_9S_2$	$Mn_2Tb_2C_{42}H_{51}O_{26}N_9S_2$
M_r gmol^{-1}	1553.71	1560.37	1586.39	1589.73
Crystal system	monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P2$_1$/c*	*P2$_1$/c*	*P2$_1$/c*	*P2$_1$/c*
a/[Å]	10.935(2)	10.906(2)	10.845(2)	10850(2)
b/[Å]	23.709(5)	23.926(5)	23.848(5)	23.920(5)
c/[Å]	12.183(2)	12.189(2)	12.151(2)	12.130(2)
α/[°]	90	90	90	90
β/[°]	113.69(3)	113.68(3)	113.35(3)	113.36(3)
γ/[°]	90	90	90	90
V/[Å^3]	2892.4(11)	2912.8(12)	2885.2(11)	2890.2(10)
T/K	100(2)	100(2)	100(2)	100(2)
Z	2	2	2	2
$\rho_{, calc}$ [g cm^{-3}]	1.781	1.776	1.823	1.823
Λ^B/ [Å]	0.71079	0.71079	0.71079	0.71079
Data Measured	17915	36088	36431	18892
Ind. Reflns	4941	5074	4922	5022
R_{int}	0.0700	0.0427	0.0888	0.0370
Reflns with I > 2σ(I)	4044	4899	4771	4746
Parameters	408	420	421	420
Restraints	95	64	64	64
R_1^C(obs), wR_2^C (all)	0.0924, 0.2365	0.0657, 0.1469	0.0516, 0.1307	0.0610, 0.1373
goodness of fit	1.081	1.195	1.131	1.222
Largest residuals/[e Å^{-3}]	2.522, -2.003	2.657, -1.866	1.384, -1.667	1.328, -2.056

	5
Formula[A]	$Mn_2Dy_2C_{42}H_{51}O_{26}N_9S_2$
M_r gmol^{-1}	1596.89
Crystal system	monoclinic
Space group	*P2$_1$/c*
a/[Å]	10.842(2)
b/[Å]	23.762(5)
c/[Å]	12.108(2)
α/[°]	90
β/[°]	113.12(3)
γ/[°]	90
V/[Å^3]	2868.7(11)
T/K	100(2)
Z	2
$\rho_{, calc}$ [g cm^{-3}]	1.845
Λ^B/ [Å]	0.71079
Data Measured	18492
Ind. Reflns	4732
R_{int}	0.0319
Reflns with I > 2σ(I)	4626
Parameters	421

Restraints	64
R_1[C](obs), wR_2[C] (all)	0.0570, 0.1319
goodness of fit	1.230
Largest residuals/[e Å $^{-3}$]	1.959, -1.730

[A] Including solvate molecules. [B] Graphite monochromator.

[C] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

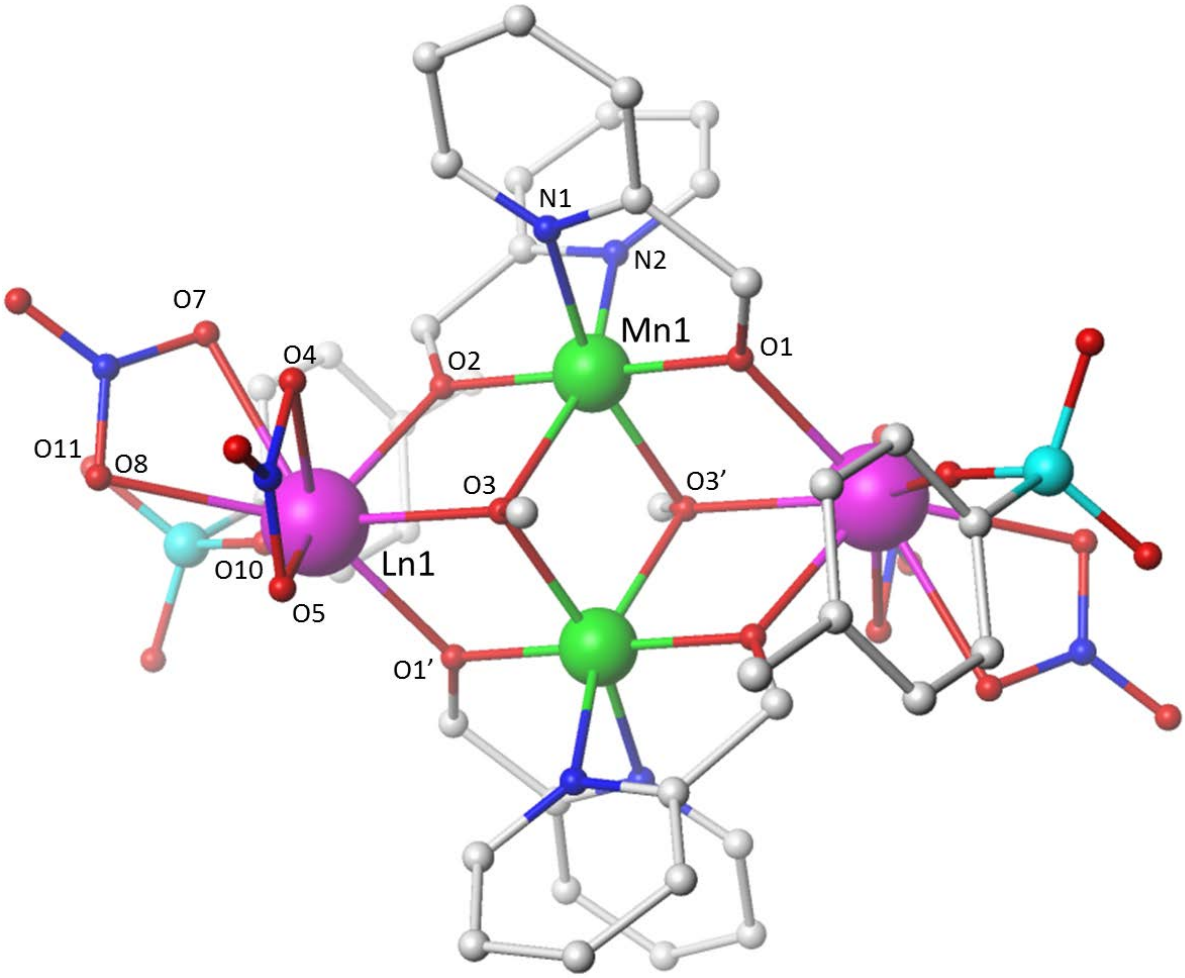


Table S2. Selected bond distances (Å) and angles (°) for complexes **1** – **5**, using the labelling scheme shown above.

	1	**2**	**3**	**4**	**5**
Ln1-O10	2.393(9)	2.393(6)	2.339(5)	2.327(6)	2.315(6)
Ln1-O11’	2.438(7)[I]	2.417(6)[I]	2.381(5)[II]	2.373(6)[I]	2.363(6)[I]
Ln1-O1’	2.445(9)[I]	2.428(6)[I]	2.373(4)[II]	2.356(6)[I]	2.339(6)[I]

Ln1-O2	2.446(8)	2.417(5)	2.377(5)	2.357(6)	2.332(5)
Ln1-O5	2.487(17)	2.489(9)	2.508(6)	2.449(8)	2.440(9)
Ln1-O3/O3x (*)	2.55(4)	2.51(4)	2.465(3)	2.440(5)	2.425(4)
Ln1-O7	2.551(10)	2.549(6)	2.500(5)	2.510(7)	2.506(7)
Ln1-O4	2.558(14)	2.563(8)	2.451(7)	2.513(8)	2.503(8)
Ln1-O8	2.575(8)	2.553(6)	2.513(5)	2.478(6)	2.474(6)
Mn1-O3'/O3x (*)	1.936(2)^{I}	2.015(3)^{I}	1.992(5)^{II}	1.984(4)^{I}	2.015(3)^{I}
Mn1-O1	1.901(7)	1.898(6)	1.906(5)	1.906(6)	1.899(6)
Mn1-O2	1.909(8)	1.904(6)	1.889(5)	1.920(6)	1.922(6)
Mn1-N1	2.064(12)	2.064(8)	2.188(6)	2.059(8)	2.084(8)
Mn1-N2	2.174(11)	2.182(7)	2.062(6)	2.193(7)	2.172(8)
Mn1-O3/O3x (*)	2.2035(3)	2.190(3)	2.185(3)	2.215(5)	2.163(4)
Mn1···Mn1$^{'}$	3.166(3)	3.147(4)	3.112(4)	3.133(3)	3.081(3)
Ln1···Mn1	3.632(2)	3.614(4)	3.481(4)	3.570(4)	3.530(4)
Ln1···Mn1'	3.571(2)	3.544(4)	3.567(4)	3.487(4)	3.468(4)
Mn1-O3/O3x-Mn1 (*)	98.395(2)	96.91(2)	96.72(2)	96.51(2)	95.42(2)

Symmetry transformation: (I) - x, - y, - z; (II) 1 - x, 1 - y, 1 – z.

(*) It was found that a methoxide and hydroxide bridging ligand occupy the same site throughout the crystal, modelled at 50:50 occupancy. The astrix denotes an average bond distance and angle from the two ligands.

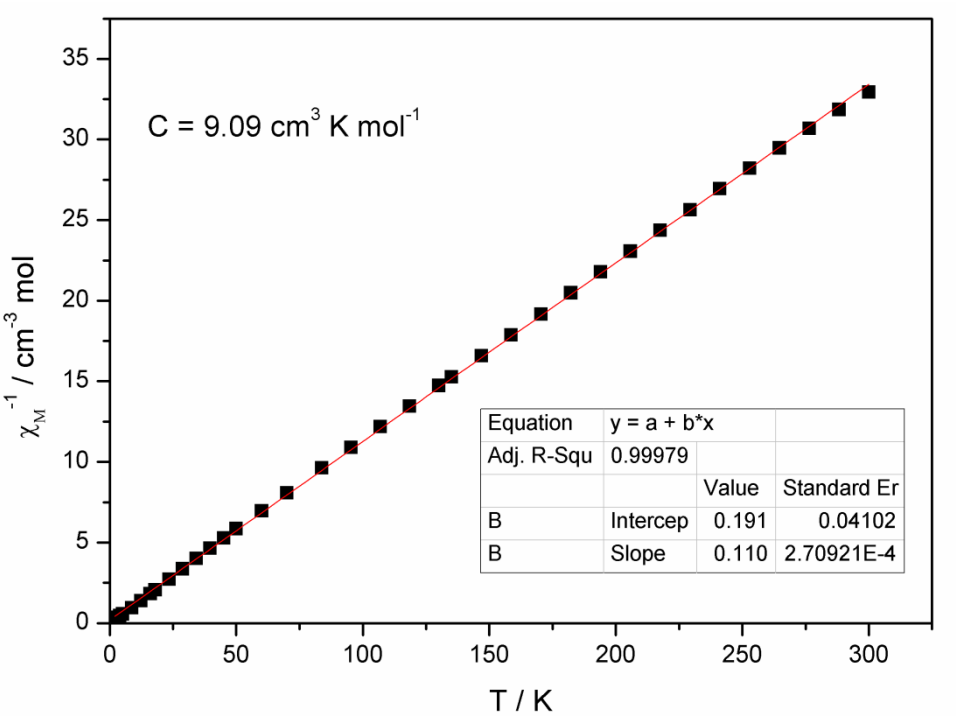


Figure S1. $1/\chi_M$ versus T for **1**.

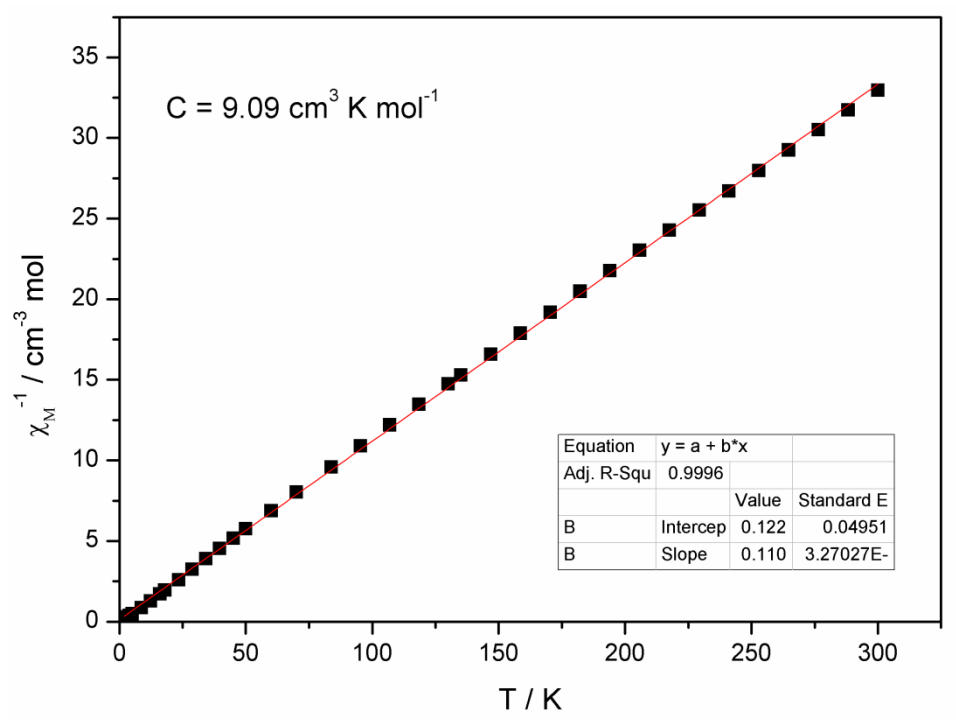


Figure S2. $1/\chi_M$ versus T for **2**.

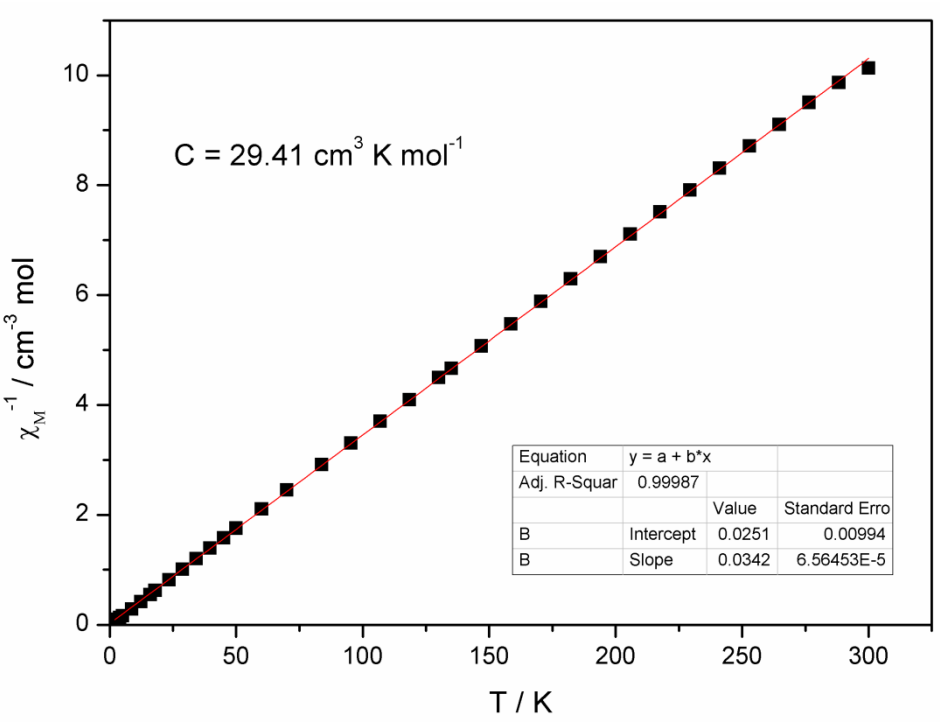


Figure S3. $1/\chi_M$ versus T for **3**.

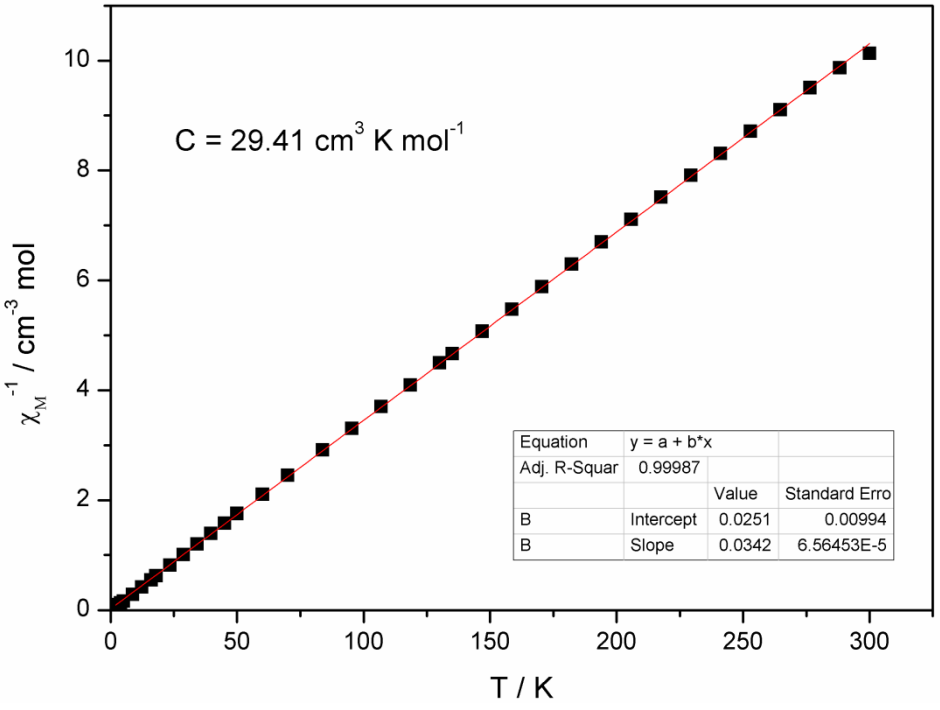


Figure S4. $1/\chi_M$ versus T for **4**.

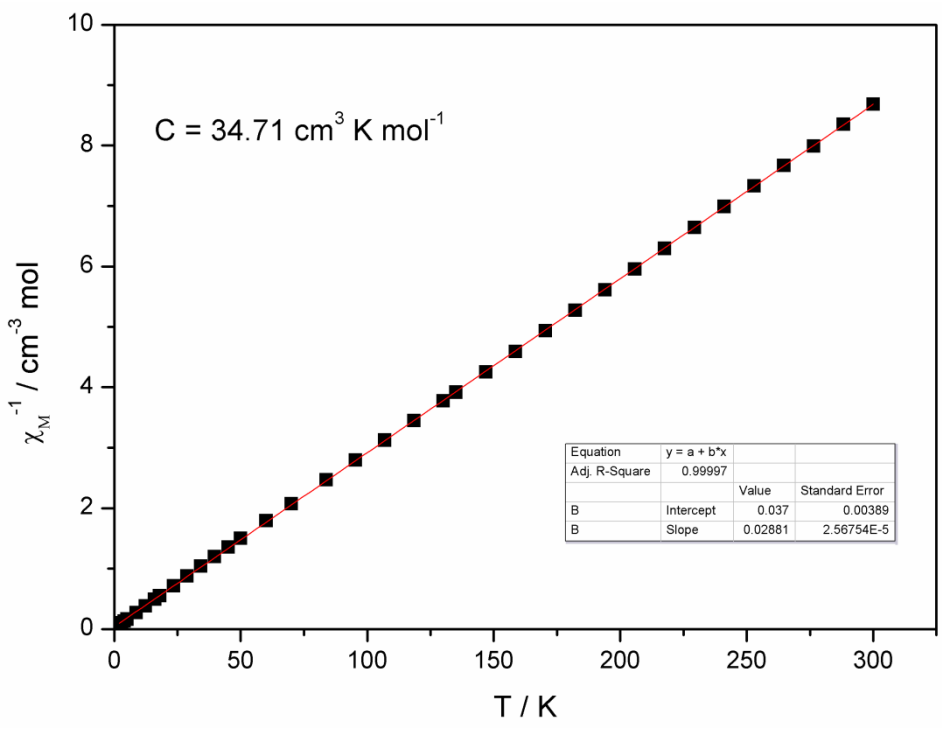
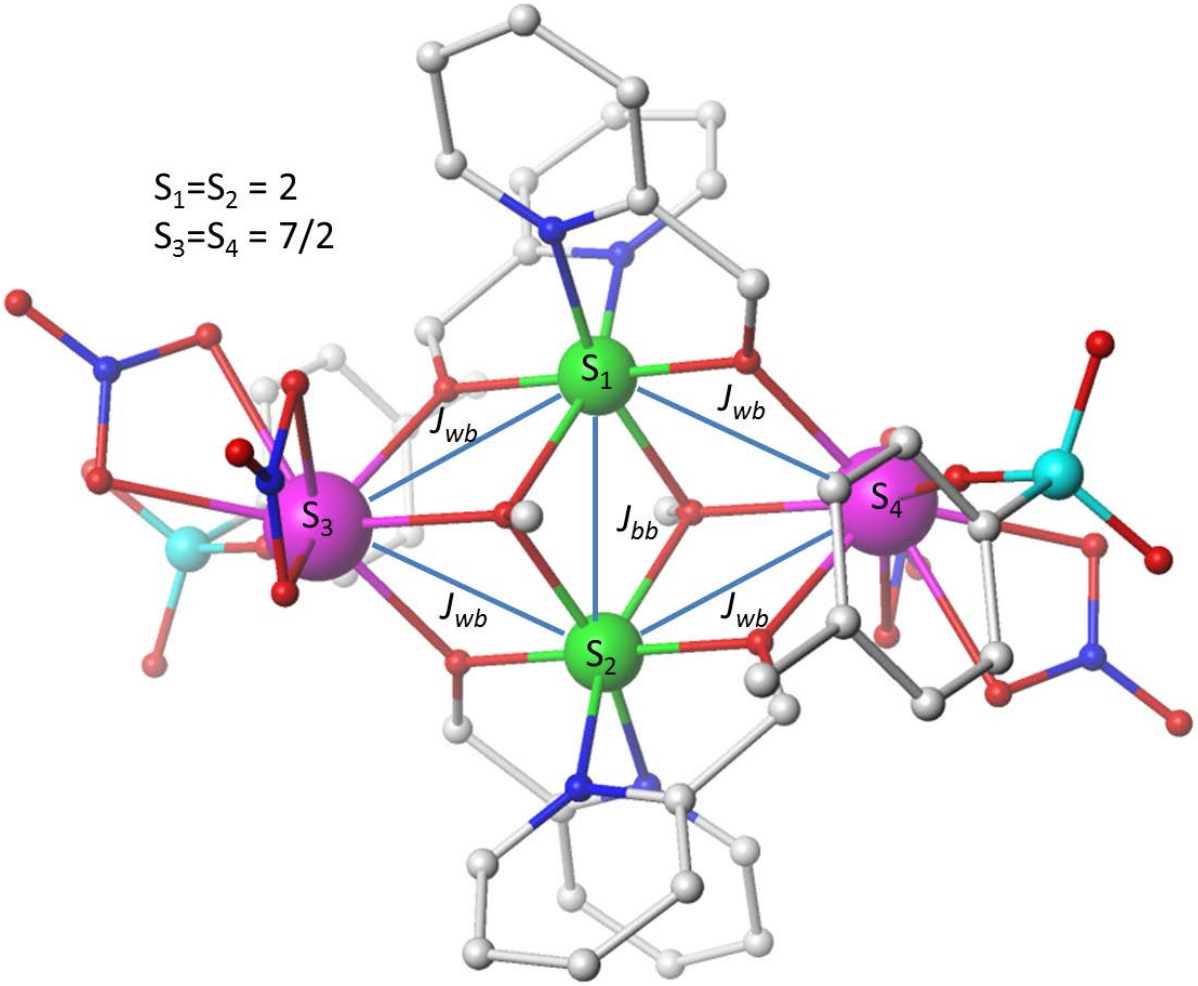


Figure S5. $1/\chi_M$ versus T for **5**.



$$\hat{H} = -2J_{bb}(\hat{S}_1\hat{S}_2) - 2J_{wb}(\hat{S}_1\hat{S}_3 + \hat{S}_1\hat{S}_4 + \hat{S}_2\hat{S}_3 + \hat{S}_2\hat{S}_4)$$

Figure S6. Magnetic exchange coupling scheme used for fitting the magnetic data for complex **3**.