Evolution of the Structures and Magnetic Properties of the Manganese Dicarboxylates, $Mn_2(CO_2(CH_2)_nCO_2)(OH)_2$ and $Mn_4(CO_2(CH_2)_nCO_2)_3(OH)_2$

Electronic Supplementary Information

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Table S1 Synthetic conditions used to make single crystals of the compounds described in this work.

Compound	Temperature (°C)	Reaction mixture ($MnCl_2 \cdot 4H_2O$:ligand :KOH:water)
$Mn_2(C_2O_4)(OH)_2$ (**1**)	200	1:1.5:3.75:200
$Mn_2(C_4H_4O_4)(OH)_2$ (**2**)	180	1:1.5:5:200
$Mn_2(C_6H_8O_4)(OH)_2$ (**3**)	125	1:1.5:5:200
$Mn_2(C_7H_{10}O_4)(OH)_2$ (**4**)	125	1:1.5:5:200
$Mn_4(C_5H_6O_4)_3(OH)_2$ (**5**)	125	1:1.5:3.75:100
$Mn_4(C_7H_{10}O_4)_3(OH)_2$ (**6**)	200	4:1:5:100

Structural Determination

Single crystal X-ray diffraction data were collected using one of three instruments with all measurements carried out at 120 K (see Table S2 and S3 for crystallographic details). Data for compounds **1** and **6** were collected on an Oxford Diffraction Gemini Ultra diffractometer equipped with an Eos CCD detector with crystals mounted on a cryoloop. Absorption corrections were carried out for these samples using analytical methods implemented in Crysalis Pro.[1] Data for **1** were collected using Mo K_α radiation (λ = 0.71073 Å), while a Cu K_α source (λ = 1.5418 Å) with multilayer optics was used for the collection of data from compound **6**. Data for compounds **2-5** were collected using Bruker-Nonius Kappa diffractometers equipped with a Mo K_α Bruker-Nonius FR591 rotating anode X-ray generator, with an instrument equipped with confocal mirrors being employed for **3-5**. Data collection for **2** was done using a Bruker-Nonius Roper CCD camera while a Bruker Apex II CCD detector was used for compounds **3-5**. The crystals from which data were collected for compounds **2-5** were all non-merohedrally twinned. Compounds **2** and **3** were twinned about the direct axis (001), **4** around the $(\bar{1}00)$ direct axis and **5** around the (100) axis. Absorption corrections for **2-5** were carried out semi-empirically using SADABS.[2] All structures were solved using direct methods and subsequently refined against $|F|^2$ using SHELX-97[3] via the Win-GX interface.[4] The displacement parameters of all non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms attached to the dicarboxylate ligands were geometrically constrained using the AFIX commands in SHELX-97. The hydroxy hydrogen atoms were readily located from the Fourier difference map and were restrained to have a bond distance of 0.85 Å to the oxygen atoms to which they are attached. These ligands are assigned as being hydroxide groups, rather than water molecules, as this is required to achieve overall charge neutrality and only one hydrogen position could be located for each oxygen atom. These oxygen atoms all bond to three metal cations and their hydrogen in a tetrahedral arrangement confirming this assignment. The isotropic thermal parameters of the hydrogen atoms were constrained to be 1.2 times the carbon or 1.5 times the oxygen to which they were attached. The residual factors are slightly higher than ideal for compounds **4-6**; most likely due to the weaker diffraction from the small crystals available of these samples.

Table S2 Crystallographic data for structure **1-3** determined using single crystal X-ray diffraction.

Compound	**1**	**2**	**3**
Formula	$Mn_3C_3H_3O_9$	$MnC_2H_3O_3$	$Mn_2C_6H_{10}O_6$
Formula Weight	347.87	129.985	288.02
Colour	Colourless	Colourless	Colourless
T (K)	120	120	120
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/n$ (14)	$P2_1/a$ (14)	$P2_1/a$ (14)
a (Å)	10.9072(5)	5.8745(3)	8.1023(2)
b (Å)	5.7181(2)	7.4316(5)	9.3777(3)
c (Å)	12.6330(5)	7.9227(5)	12.5161(4)
α (°)	90	90	90
β (°)	108.259(5)	92.414(4)	103.948(2)
γ (°)	90	90	90
V (Å^3)	748.23(5)	345.57(4)	922.94(5)
Z	4	4	4
ρ_{calc} (g cm^{-3})	3.088	2.498	2.073
μ (cm^{-1})	5.015	3.637	2.735
Refl. Meas./Unique	5302/1764 [R_{int} = 0.0374]	5609/794 [R_{int} =0.0680]	9994/2098 [R_{int} = 0.0413]
Parameters Refined	145	60	134
$R1$, $wR2^a$ (all)	0.0674, 0.0797	0.0434, 0.0707	0.0367, 0.0755
$R1$, $wR2^a$ (obs)	0.0348, 0.0648	0.0302, 0.0669	0.0337, 0.0730
χ^2	1.023	1.197	1.185

Table S3 Crystallographic data for structures **4-6** determined by single crystal X-ray diffraction.

Compound	**4**	**5**	**6**
Empirical Formula	$Mn_2C_7H_{12}O_6$	$Mn_4C_{15}H_{20}O_{14}$	$Mn_4C_{21}H_{32}O_{14}$
Formula Weight	302.05	644.07	728.23
Colour	Colourless	Colourless	Colourless
T (K)	120	120	120
Crystal System	Monoclinic	Triclinic	Triclinic
Space Group	$P2_1/a$ (14)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a (Å)	8.1123(10)	5.0589(2)	5.0585(3)
b (Å)	9.3629(11)	10.5756(6)	12.4647(7)
c (Å)	13.4620(18)	19.1948(8)	20.8241(9)
α (°)	90	79.883(3)	90.848(4)
β (°)	94.880(7)	87.442(3)	90.047(4)
γ (°)	90	85.762(3)	90.770(5)
V (Å^3)	1018.8(2)	1007.68(8)	1312.75(12)
Z	4	2	2
ρ_{calc} (g cm^{-3})	1.969	2.123	1.848
μ (cm^{-1})	2.483	2.525	15.901
Refl. Meas./Unique	7828/2330 [R_{int} =0.0555]	16405/4576 [R_{int} = 0.0552]	8448/4906 [R_{int} = 0.0552]
Parameters Refined	144	305	358
$R1$, $wR2^a$ (all)	0.0992, 0.2520	0.0788, 0.1697	0.0807, 0.2035
$R1$, $wR2^a$ (obs)	0.0915, 0.2423	0.0667, 0.1580	0.0709, 0.1955
χ^2	1.142	1.131	1.127

[a] $w = 1/\left[\sigma^2\left(F_o^2\right) + \left(aP\right)^2 + bP\right]$ and $P = \left(\max\left(F_o^2, 0\right) + 2F_c^2\right)/3$; $R1 = \sum\left\|F_o\right| - \left|F_c\right\| / \sum\left|F_o\right|$ and $wR2 = \sqrt{\left\{\sum\left[w\left(F_o^2 - F_c^2\right)^2\right] / \sum w\left(F_o^2\right)^2\right\}}$

Physical Measurements

Infra-red spectra were collected over the range of 4000-500 cm^{-1} on a Bruker Tensor-27 ATR spectrometer. The spectrum of **2** exhibited the following features: ν_{max}/cm^{-1} 3617 (OH), 2970 and 2911 cm^{-1} (CH_2); 1554 (ν_{as} CO_2^-); 1450 (CH_2); 1415 (ν_s CO_2^-); 1386 and 1221(C-O); 1149 (ν_{as} C-C); and 933, 887, 803, 740, 689, 658, 617 and 559 (metal-oxygen bonding and C-H).[5] Thermogravimetric analysis (TGA) was performed in air on a TA instruments Q500 using a heating rate of 10 °C/minute. DC magnetic susceptibility measurements were made with a Quantum Design Squid magnetometer with various applied fields. AC magnetic susceptibility measurements were also made using a SQUID but with 5 Oersted ampltitude.

Table S4 Selected Mn-O bond distances (Å) in compounds **1**, **2**, **3** and **4**.

1		Mn3-O2H	2.130(3)	**3**		**4**	
Mn1-O1H	2.104(3)	Mn3-O2H	2.142(3)	Mn1-O1H	2.081(2)	Mn1-O1H	2.064(6)
Mn1-O3H	2.137(3)	Mn3-O1H	2.215(3)	Mn1-O1	2.094(2)	Mn1-O1	2.087(6)
Mn1-O3H	2.143(3)	Mn3-O6	2.233(2)	Mn1-O2H	2.095(2)	Mn1-O2H	2.094(6)
Mn1-O2	2.256(3)	Mn3-O1	2.235(3)	Mn1-O3	2.165(2)	Mn1-O3	2.160(6)
Mn1-O2	2.322(3)	Mn3-O3	2.260(3)	Mn1-O2H	2.208(2)	Mn1-O2H	2.210(5)
Mn1-O4	2.342(3)	**2**		Mn2-O1H	2.157(2)	Mn2-O1H	2.160(6)
Mn2-O3H	2.131(3)	Mn1-O2	2.152(2)	Mn2-O4	2.162(2)	Mn2-O4	2.162(6)
Mn2-O1H	2.148(3)	Mn1-O1H	2.163(3)	Mn2-O2	2.164(2)	Mn2-O2	2.170(6)
Mn2-O2H	2.172(3)	Mn1-O1H	2.164(3)	Mn2-O2H	2.177(2)	Mn2-O2H	2.184(5)
Mn2-O3	2.241(2)	Mn1-O1H	2.173(2)	Mn2-O1H	2.211(2)	Mn2-O1H	2.215(6)
Mn2-O5	2.273(3)	Mn1-O1	2.215(2)	Mn2-O3	2.269(2)	Mn2-O3	2.276(6)
Mn2-O6	2.285(3)	Mn1-O1	2.330(3)				

Table S5 Selected Mn-O bond distances (Å) in compounds **5** and **6**.

5				**6**			
Mn1-O11	2.088(5)	Mn3-O21	2.084(5)	Mn1-O11	2.094(5)	Mn3-O21	2.095(5)
Mn1-O2H	2.112(4)	Mn3-O1H	2.121(4)	Mn1-O1	2.099(5)	Mn3-O1H	2.121(5)
Mn1-O1	2.116(5)	Mn3-O22	2.125(4)	Mn1-O2H	2.117(5)	Mn3-O22	2.129(5)
Mn1-O12	2.131(5)	Mn3-O4	2.134(5)	Mn1-O12	2.135(5)	Mn3-O4	2.168(5)
Mn1-O14	2.214(4)	Mn3-O24	2.205(4)	Mn1-O14	2.184(5)	Mn3-O24	2.208(5)
Mn2-O13	2.120(4)	Mn4-O23	2.117(5)	Mn2-O1H	2.129(5)	Mn4-O23	2.130(5)
Mn2-O1H	2.137(4)	Mn4-O2H	2.153(4)	Mn2-O13	2.143(5)	Mn4-O2H	2.150(5)
Mn2-O2H	2.188(4)	Mn4-O1H	2.172(4)	Mn2-O3	2.186(5)	Mn4-O24	2.189(5)
Mn2-O3	2.197(4)	Mn4-O24	2.187(4)	Mn2-O14	2.201(5)	Mn4-O1H	2.196(5)
Mn2-O14	2.204(4)	Mn4-O2	2.203(4)	Mn2-O2H	2.221(5)	Mn4-O2	2.235(5)
Mn2-O12	2.301(4)	Mn4-O22	2.355(4)	Mn2-O12	2.255(5)	Mn4-O22	2.322(5)

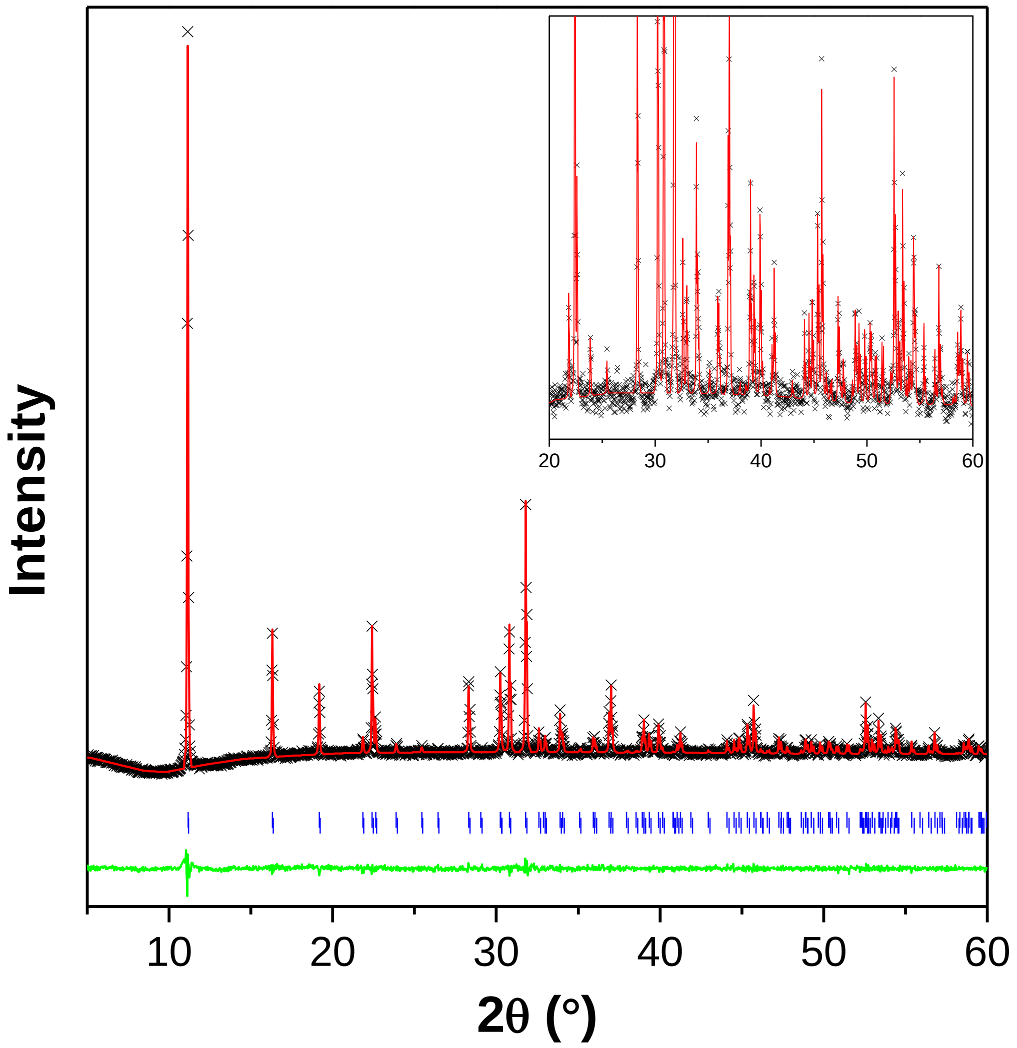

Fig. S1 Room temperature X-ray diffraction pattern of a sample of compound **2** indicating its purity, fitted using the Le Bail method. The crosses, and upper and lower continuous lines are the experimental, calculated and difference profiles, respectively. The insert shows the higher angle reflections in more detail. The vertical markers indicate the allowed Bragg reflections. The final R_p, R_{wp} and χ^2 values are 2.1 %, 2.8 % and 1.5 and the cell parameters were determined to be a = 5.9108(1) Å, b = 7.4486(2) Å, c = 7.9395(2) Å and β = 92.880(2)°.

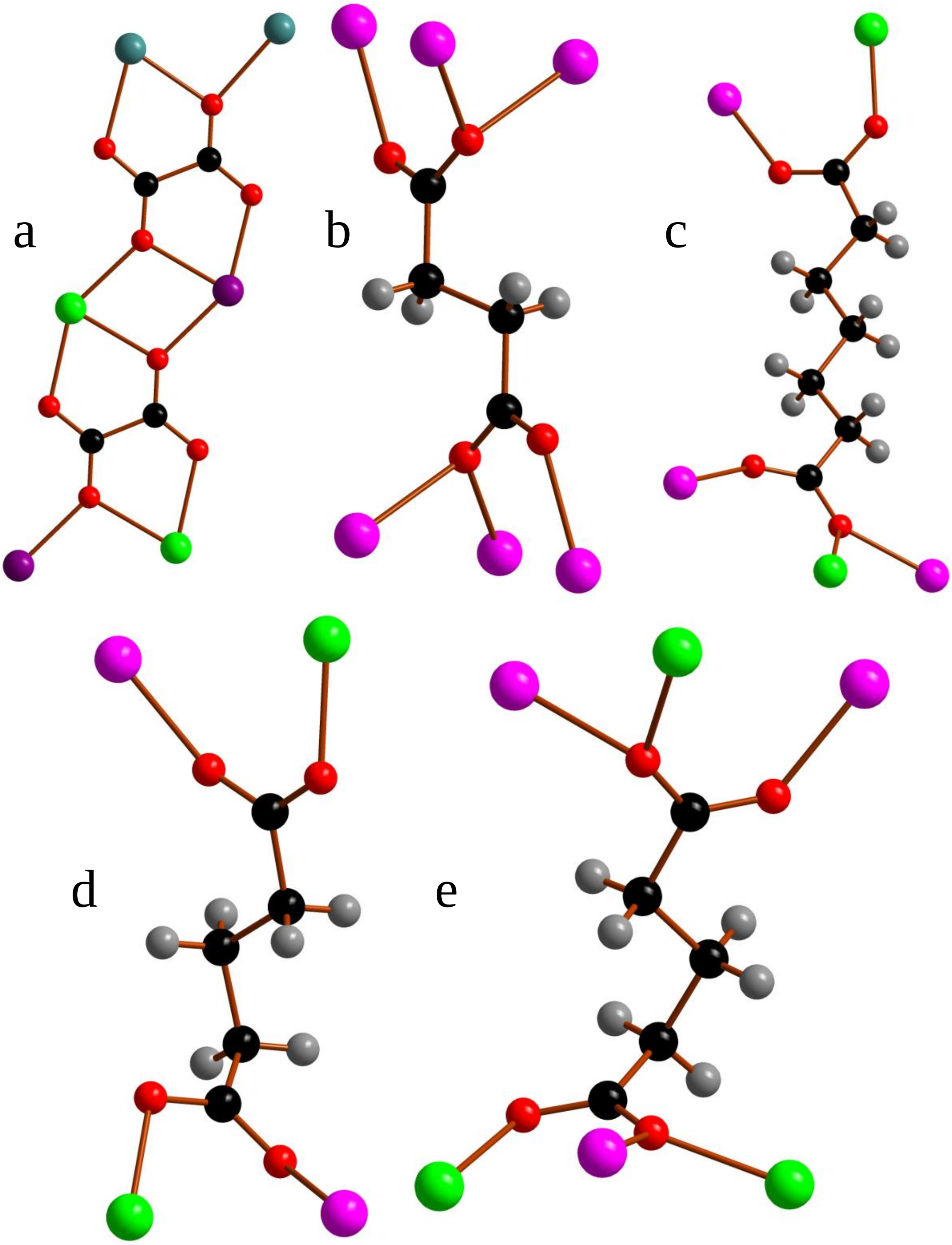

Fig. S2 Illustration of the coordination modes of the ligands in compounds a) **1**, b) **2**, c) **3** and **4**, and d) and e), **5** and **6**. Compounds **1** and **2** have dicarboxylates featuring (1212) connectivity and **4** and **5** have (1112) bridging. Ligands in **3** and **6** exhibit two types of coordination environments; one with (1111) and two with (1212) connectivity. All colours are the same as those used in the main article.

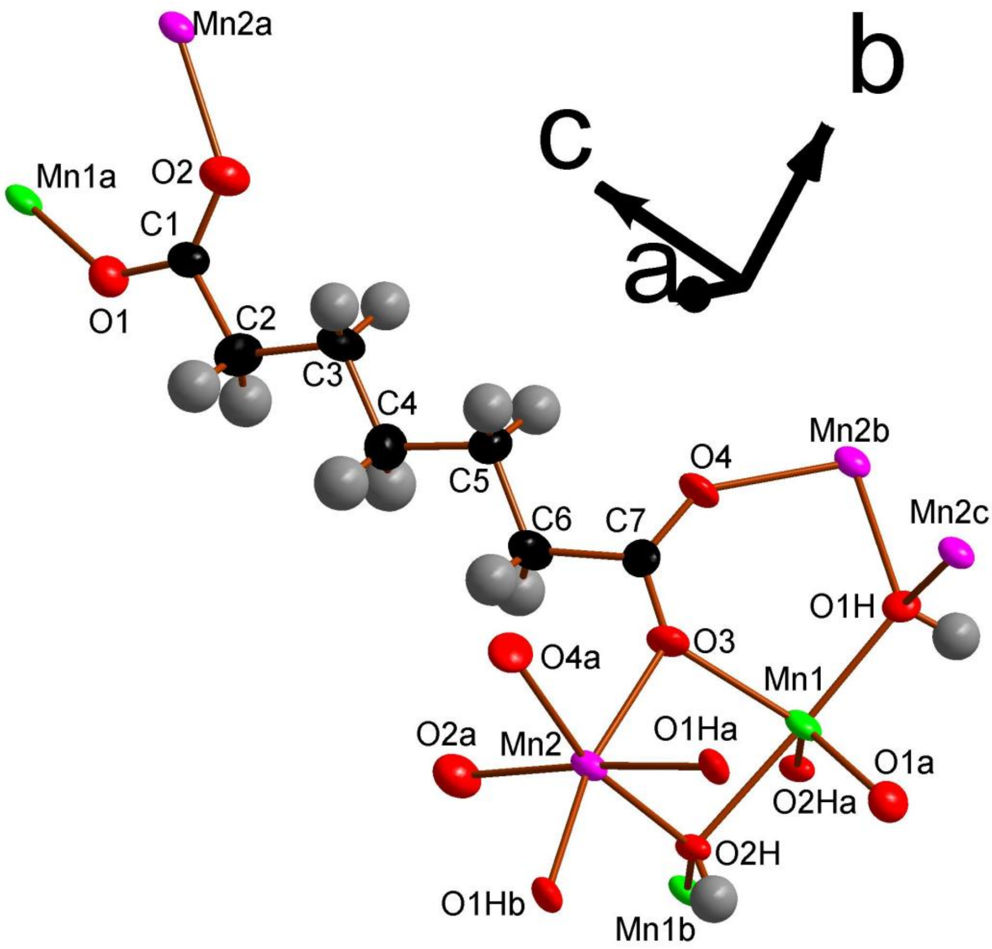

Fig. S3 The asymmetric unit of framework **4** with 80 % probability ellipsoids. The labels on the hydrogen atoms are omitted for the sake of clarity. Additional non-hydrogen atoms, included to illustrate the coordination sphere of all atoms in the structure, are shown and labelled alphabetically.

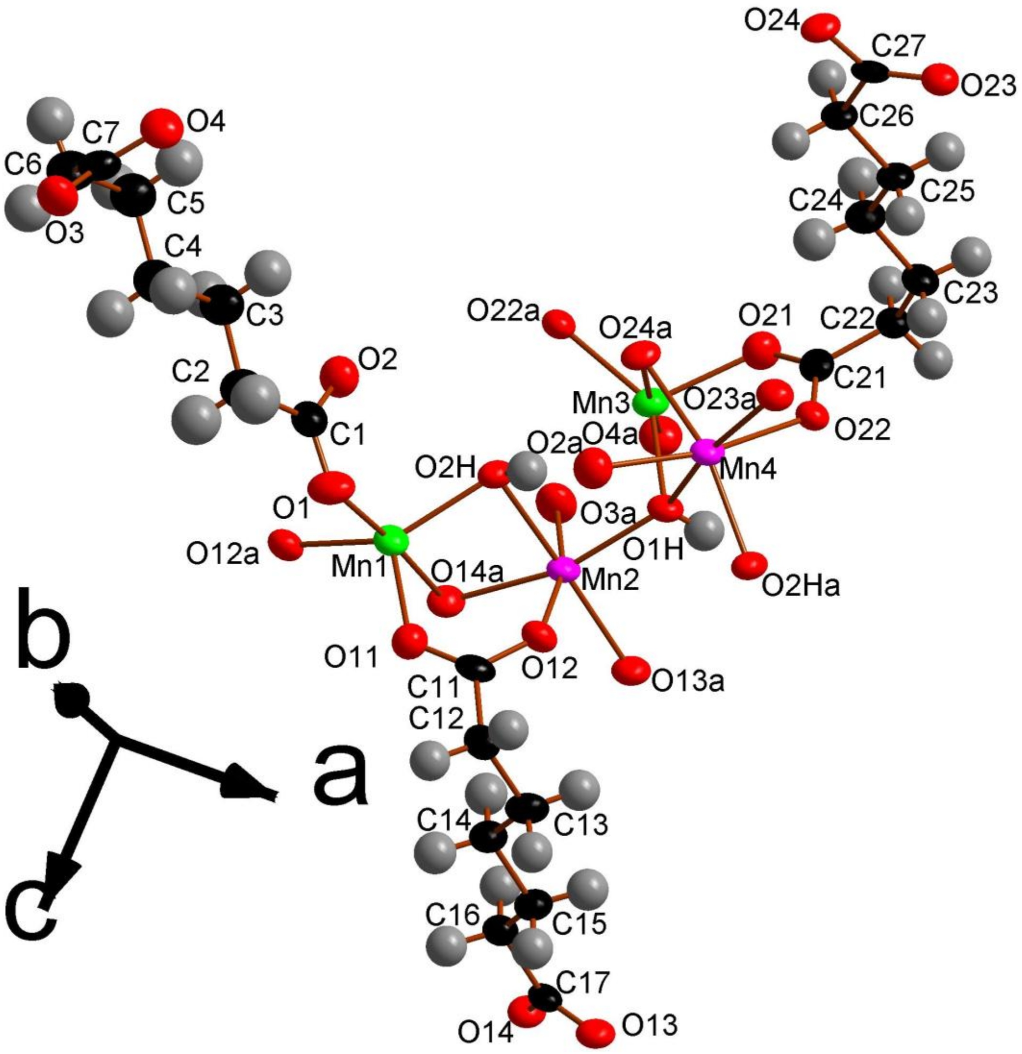

Fig. S4 Depiction of the asymmetric unit of framework **6** with 80 % probability ellipsoids. The labels on the hydrogen atoms are omitted for the sake of clarity. Additional non-hydrogen atoms, included to illustrate the coordination sphere of all cations in the structure, are shown and labelled alphabetically.

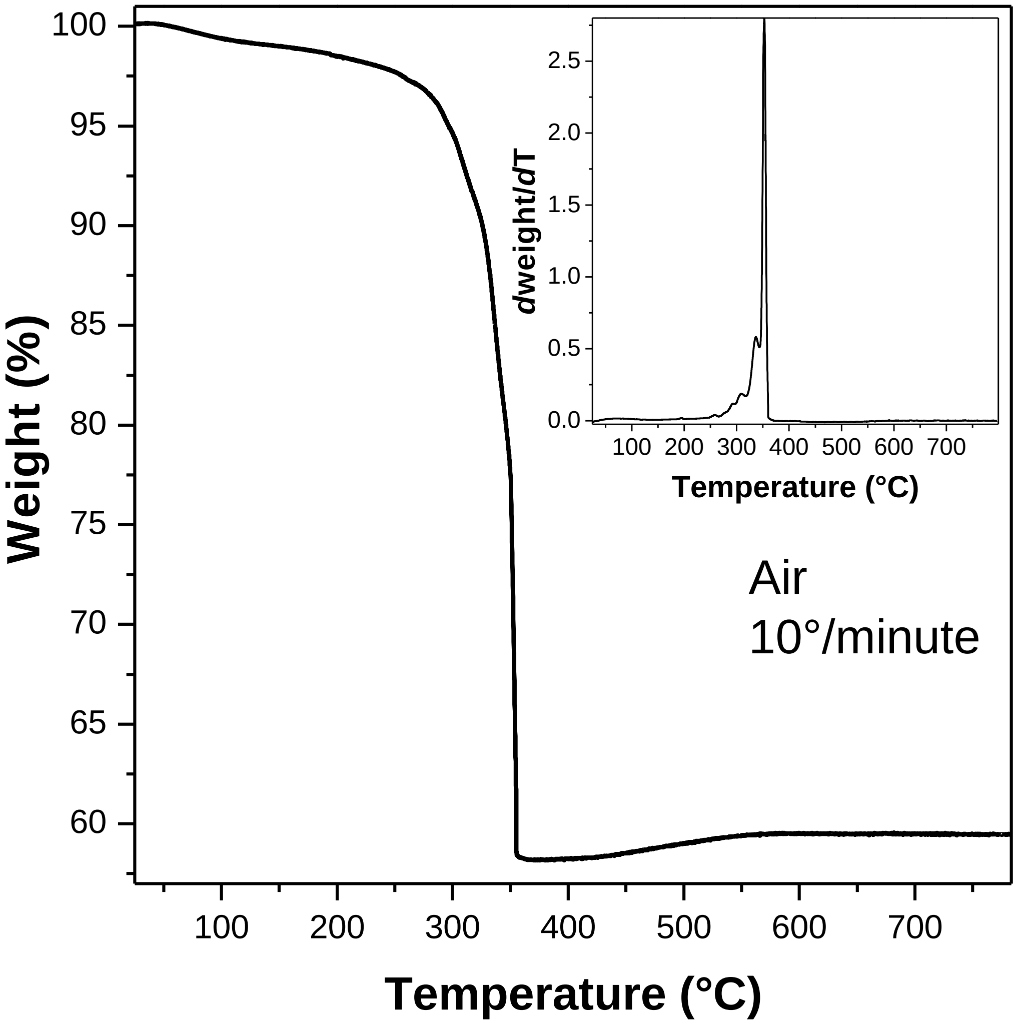

Fig. S5 Plot of weight, expressed as a percentage of intial weight, versus temperature for compound **2** determined using TGA. The insert shows the change in the derivative of weight with temperature.

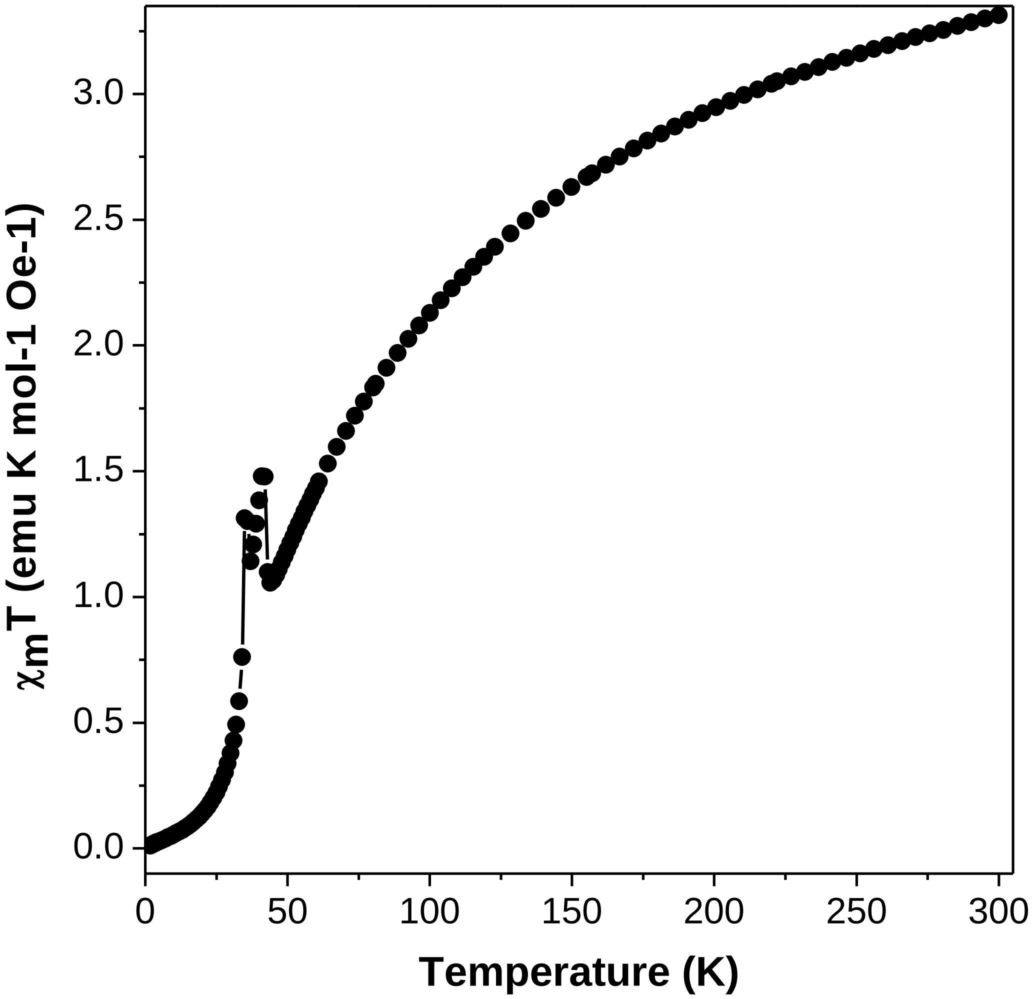

Fig. S6 Plot of χ_mT versus temperature from ZFC measurements in a 100 Oe field.

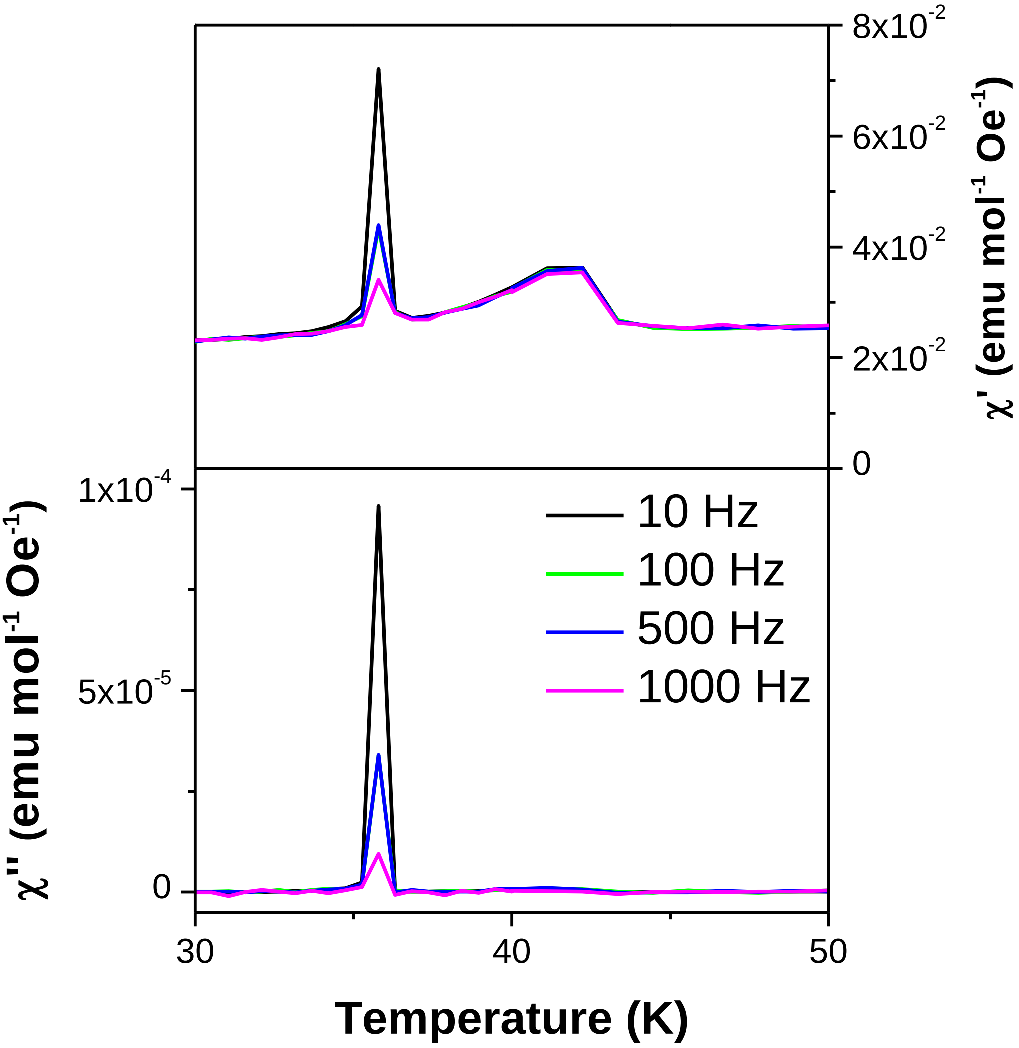

Fig. S7 Plot of AC magnetic susceptibility of compound **2**.

1. Oxford Diffraction, *CrysAlis PRO*, (2010) Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
2. G. M. Sheldrick, *SADABS*, (2007) Bruker AXS Inc., Madison, Wisconsin, USA.
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