

Synthesis and characterization of homo- and heterovalent tetra- hexa- hepta- and decanuclear manganese clusters using pyridyl functionalized β -diketone, carboxylate and triethanolamine ligands†‡

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The syntheses and characterizations are reported for six new homo- and heterovalent manganese clusters, utilizing pyridyl functionalized β -diketones ligands. The reaction of the trinuclear complex $[\text{Mn}_3\text{O}(\text{O}_2\text{CPh})_6(\text{H}_2\text{O})(\text{Py})_2]$ with 1,3-di(pyridine-2-yl)propane-1,3-dione (dppdH) in CH_2Cl_2 resulted in a mixed-valence $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ decanuclear cluster of formula $[\text{Mn}_{10}\text{O}_7(\text{dppd})_3(\text{O}_2\text{CPh})_{11}]\cdot 4\text{CH}_2\text{Cl}_2$ (**1**). The structure of the core of **1** is based upon a centred tricapped trigonal prism. Reacting $\text{Mn}(\text{BF}_4)_2\cdot x\text{H}_2\text{O}$ with dppdH and triethylamine (NEt_3) in $\text{CH}_2\text{Cl}_2\text{--MeOH}$ gave a rare, homoleptic hexanuclear cluster of formula $[\text{Mn}^{\text{II}}_6(\text{dppd})_8][\text{BF}_4]_4$ (**2**) which has a triangular based core. Reaction of $\text{Mn}(\text{Y})_2\cdot x\text{H}_2\text{O}$, $\text{Y} = \text{NO}_3^-$ or BF_4^- , with dppdH or 1-phenyl-3-(2-pyridyl)propane-1,3-dione (pppdH) in the presence of triethanolamine (teaH_3) and NEt_3 gave a heptanuclear 'disc' like manganese core of general formula $[\text{Mn}^{\text{II}}_7(\text{X})_6(\text{tea}(\text{OH})_3)[\text{Y}]_2\cdot\text{solv}]$ (**3**) $\text{X} = \text{pppd}^-$ or dppd^- and $\text{Y} = \text{NO}_3^-$ or BF_4^- . The addition of N-(2-pyridinyl)acetoacetamide (paaH) to $\text{Mn}(\text{Y})_2\cdot 4\text{H}_2\text{O}$ $\text{Y} = \text{NO}_3^-$ or ClO_4^- in MeOH gave a second divalent heptanuclear cluster with a 'disc'-like core of general formula $[\text{Mn}_7(\text{paa})_6(\text{OMe})_6][\text{X}]_2\cdot\text{solv}$ (**4**) ($\text{X} = \text{NO}_3^-$ or ClO_4^-), whilst the addition of paaH to a mixture of $\text{Mn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$, teaH_3 and NEt_3 in $\text{CH}_2\text{Cl}_2\text{--MeOH}$ resulted in the formation of a mixed-valence $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ tetranuclear 'butterfly' complex of formula $[\text{Mn}_4(\text{paa})_4(\text{teaH}_2)[\text{NO}_3]_2\cdot 2\text{MeOH}\cdot 2\text{CH}_2\text{Cl}_2]$ (**5**). Compound **5** displays the rare $\text{Mn}^{\text{II/III}}$ oxidation state distribution of the body positions being Mn^{II} while the wing tips are Mn^{III} . The *in situ* formation of the tetranuclear $[\text{Mn}_4(\text{teaH}_2)_2(\text{teaH}_2)_2(\text{O}_2\text{C}(\text{CH}_3)_3)_2][\text{O}_2\text{C}(\text{CH}_3)_3]_2$ 'butterfly' complex followed by the addition of $\text{Mn}(\text{O}_2\text{CMe})_2\cdot 4\text{H}_2\text{O}$ resulted in a mixed-valence $\text{Mn}_4^{\text{II}}\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ hexanuclear species of formula $[\text{Mn}_6\text{O}_2(\text{teaH}_2)_4(\text{O}_2\text{CMe})_4][\text{NO}_3]_2[\text{O}_2\text{CMe}]\cdot \text{CH}_2\text{Cl}_2\cdot \text{MeOH}\cdot 2\text{H}_2\text{O}$ (**6**). The core of **6** displays a face sharing dicubane topology. Compounds **1** and **6** both display novel trapped-valence metal cores containing three different oxidation states on the manganese ion. Compounds **1**, **2** and **3** are the first manganese based dppd clusters, while **4** and **5** are the first with the pyridylamino-substituted β -diketone ligand (paaH). The magnetic data for **1**, **2**, **3**, **4**, and **6** are dominated by antiferromagnetic interactions within the clusters, leading to small ground spin values of $S = 1$ for **1**, $S = 3$ for **2**, $S = 5/2$ for **3**, $S = 5/2$ for **4** and $S = 1/2$ for **6**. Compound **5**, however, displays overall ferromagnetic interactions with the data indicating an $S = 6$ ground state. **5** also exhibits probable single molecule magnet behaviour as indicated by frequency dependent out-of-phase χ_M'' peaks in the AC susceptibility measurements.

Introduction

The search for new polynuclear transition metal complexes containing manganese¹ in its various oxidation states that includes

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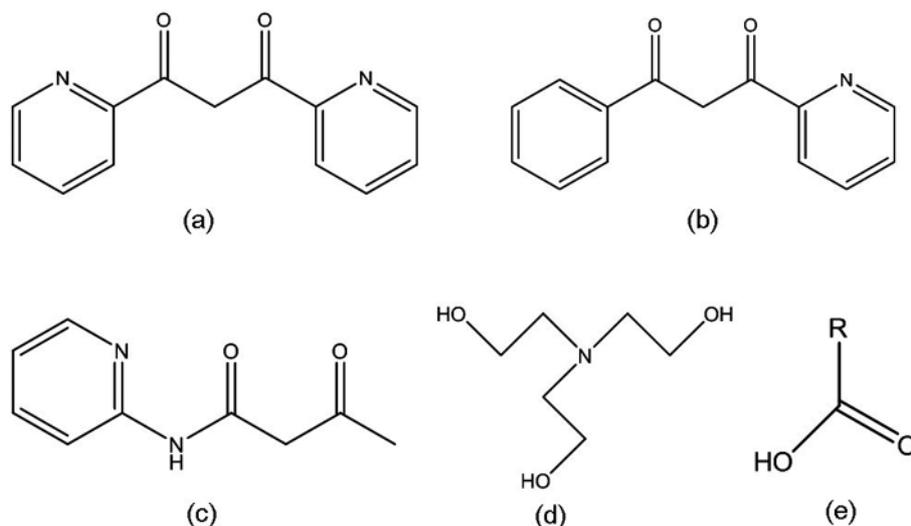
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† Structural aspects of this research were undertaken on the MX2 beamline at the Australian Synchrotron, Clayton, Victoria, Australia.

‡ Electronic supplementary information (ESI) available: Experimental aspects for **3a**, **3b** and **4a**; Tables S1–S6, bond-valence sums for **1–6**; Tables S7–S12, selected bond lengths for **1–6**; Figs. S1–S5, crystal packing diagrams for **3**, **4**, **4a**, **5** and **6**; Figs. S6, S7, S9, S10, S12–S18, plots of DC and AC susceptibilities for **1–6**; Figs. S8 and S11, fits and coupling schemes for **2**, **3**, and **4**. CCDC reference numbers 768051–768056. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00054j

Mn^{III} , stems from the realization that these clusters can behave as single molecule magnets (SMMs).² Single molecule magnets derive their properties from having a large ground spin state (S) with a sufficiently large magnetic anisotropy due to a negative axial zero-field splitting (D). This leads to an appreciable barrier for magnetization reversal and thus at sufficiently low temperatures will act as a nanoscale magnet. These compounds are usually synthesized *via* a self assembly approach.³ This is a synthetic technique that utilizes a mixture of reagents such as a metal salt or a preformed 'building block' such as the $\{\text{Mn}_3\}$ oxo-centered triangles, a flexible bridging ligand or ligands, usually an added base and the reaction solvent or solvents. There are, therefore, many variables and parameters that can be adjusted so as to allow access to a range of various polynuclear compounds. Probably the most important factor is the choice of bridging ligand and in order to be able to isolate new manganese clusters that display



Scheme 1 Ligands used (a) dppdH, (b) pppdH, (c) paaH, (d) teaH₃ and (e) carboxylic acid.

SMM behaviour, it is vital to explore new ligands to help stabilize novel metal topologies.

While dipyridyl ketone has been used successfully in polynuclear manganese chemistry,⁴ much less is known on pyridyl-containing β -diketones. One recent such example reported during the course of the present study was the use of 1-phenyl-3-(2-pyridyl)propane-1,3-dione (pppdH) (Scheme 1) and 1-(2-pyridyl)-3-(p-tolyl)propane-1,3-dione to form tetra- and hexanuclear nuclear manganese complexes when reacted with oxo-centered Mn₃ carboxylate triangles.⁵ A β -diketone functionalized with a single pyridyl group was utilized in that case. In the work described here, we have employed a β -diketone functionalized with two 2-pyridyl rings, 1,3-di(pyridine-2-yl)propane-1,3-dione (dppdH) (Scheme 1), as well as simple variations of pyridyl β -diketones, including the pppdH ligand mentioned above and a β -diketone functionalized with an N-(2-pyridyl)amino group – N-(2-pyridinyl)acetamide (paaH) (Scheme 1). The dppdH ligand has been successfully used in the past in the formation of trinuclear lanthanide clusters,⁶ while paaH has been used to synthesize Cu^{II} dimeric complexes.⁷ These types of β -diketone ligands were thus utilized by us with the aim of forming novel polynuclear manganese clusters. We have also continued our triethanolamine work⁸ (teaH₃) (Scheme 1) in which we combine this flexible, alkoxo-bridging ligand with the various pyridyl substituted β -diketones mentioned above and in some cases we have also utilized certain carboxylate ligands (Scheme 1).

Experimental

All reactions were carried out under aerobic conditions using commercial grade solvents. The chemicals manganese(II) nitrate tetrahydrate, manganese(II) tetrafluoroborate hydrate, manganese(II) perchlorate hexahydrate, manganese(II) acetate tetrahydrate, triethanolamine and triethylamine were obtained from Sigma Aldrich. The ligands 1,3-di(pyridine-2-yl)propane-1,3-dione (dppdH) and 1-phenyl-3-(2-pyridyl)propane-1,3-dione (pppdH) were synthesized following the procedure reported by

Massi *et al.*⁶ The ligand N-(2-pyridinyl)acetamide (paaH) was synthesised as reported previously by Khalifa.⁹

[Mn₁₀O₇(dppd)₃(O₂CPh)₁₁].4CH₂Cl₂ (1)

[Mn₃O(O₂CPh)₆(H₂O)(Py)₂] (0.21 g, 0.25 mmol) was dissolved in 20 ml of dichloromethane (CH₂Cl₂) followed by the addition of 1,3-di(pyridine-2-yl)propane-1,3-dione (0.049 g, 0.2 mmol) which afforded a deep brown solution, after stirring for 2 h the solution was then layered with diethyl ether to give small dark brown crystals of **1** over 1 week. Yield: 173 mg, 56.3%. Anal. Calculated (found) for **1** : Mn₁₀C₁₂₀H₉₀O₃₅N₆Cl₈ : C, 47.9 (47.59); H, 3.01 (3.87); N, 2.79 (2.73). Selected IR data ATR (cm⁻¹): 3061w, 2973w, 2864w, 1614sh, 1602m, 1542s, 1462w, 1447w, 1372s, 1351sh, 1177w, 710w.

[Mn₆(dppd)₈][BF₄]₄ (2)

Mn(BF₄)₂·xH₂O (0.33 g, 1 mmol) was dissolved in 20 ml of a 10:1 CH₂Cl₂–MeOH mixture followed by the addition of 1,3-di(pyridine-2-yl)propane-1,3-dione (0.18 g, 1 mmol). Triethylamine (0.14 ml, 1 mmol) was then added to produce a red/orange solution and this was stirred for 2 h. This solution was then layered with hexane and left to stand. After 3 days large red hexagonal crystals of **2** had formed. Yield: 101 mg, 24.4%. Anal. Calculated (found) for **2** : Mn₆C₁₀₄H₇₂O₁₆N₁₆B₄F₁₆ : C, 50.4 (50.23); H, 2.93 (2.89); N, 9.04 (8.88). Selected IR data ATR (cm⁻¹): 3537br, 1594sh, 1551sh, 1528 s, 1447s, 1412m, 1338s, 1315w, 1225w, 1047m, 1006w, 947w, 781w, 744w, 712w.

[Mn₇(pppd)₆(tea)(OH)₃][BF₄]₂·2MeOH·2CH₂Cl₂ (3) [see the ESI† for 3a and 3b analogues]

Mn(BF₄)₂·xH₂O (0.33 g, 1 mmol) was dissolved in 20 ml of MeOH followed by the addition of 1-phenyl-3-(2-pyridyl)propane-1,3-dione (0.18 g, 1 mmol) and triethanolamine (0.13 ml, 1 mmol). Triethylamine (0.55 ml, 4 mmol) was then added to produce a deep brown solution and this was stirred for 2 h. This solution was then

evaporated down and redissolved in CH_2Cl_2 –MeOH (20 : 5 ml) and layered with diethyl ether, after 2 days red/brown crystals of **3** had formed. Yield: 79 mg, 23.7%. Anal. Calculated (found) for **3**: $\text{Mn}_7\text{C}_{94}\text{H}_{87}\text{O}_{20}\text{N}_7\text{B}_2\text{F}_8$: C, 51.49 (51.23); H, 4.00 (3.85); N, 4.47 (4.51). Selected IR data ATR (cm^{-1}): 2865w, 1594s, 1565s, 1512s, 1489w, 1465w, 1449s, 1439s, 1413s, 1283s, 1063w, 1044w, 942w, 767s, 715w, 623w.

[Mn₇(paa)₆(OMe)₆][NO₃]₂·6MeOH (4**) [see the ESI[†] for analogue **4a**]**

$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.25 g, 1 mmol) was dissolved in 20 ml of MeOH followed by the addition of N-(2-pyridinyl)acetamide (0.18 g, 1 mmol) and triethylamine (0.14 ml, 1 mmol) to produce a light brown solution which was then stirred for 10 min. Diethyl ether was then allowed to diffuse into the solution and yellow crystals of **4** had formed after 1 day. Yield: 165 mg, 61.1%. Anal. Calculated (found) for **4**: $\text{Mn}_7\text{C}_{66}\text{H}_{96}\text{O}_{30}\text{N}_{14}$: C, 40.65 (40.78); H, 4.96 (4.99); N, 10.06 (10.23). Selected IR data ATR (cm^{-1}): 3310w, 3210w, 2359w, 1636m, 1588m, 1514m, 1456s, 1406m, 1335m, 1278m, 1233m, 1198m, 1153m, 1043m, 1004m, 967w, 769w, 633w.

[Mn₄(paa)₄(teaH)₂][NO₃]₂·2MeOH·2CH₂Cl₂ (5**)**

$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.25 g, 1 mmol) was dissolved in 20 ml of a 3 : 1 MeOH– CH_2Cl_2 mixture followed by the addition of N-(2-pyridinyl)acetamide (0.18 g, 1 mmol) and triethanolamine (0.13 ml, 1 mmol). Triethylamine (0.55 ml, 4 mmol) was then added to produce a deep brown solution which was then stirred for 2 h. The solution was then left to evaporate slowly, after 3 days red/brown crystals of **5** had formed. Yield: 165 mg, 42.3%. Anal. Calculated (found) for **5**: $\text{Mn}_4\text{C}_{52}\text{H}_{74}\text{O}_{22}\text{N}_{12}\text{Cl}_4$: C, 39.51 (39.34); H, 4.72 (4.74); N, 10.63 (10.59). Selected IR data ATR (cm^{-1}): 1627w, 1592s, 1538sh, 1512s, 1464s, 1426m, 1387m, 1332m, 1296m, 1258m, 1232m, 1158w, 1059w, 1032w, 963m, 827w, 767w, 679w.

[Mn₆O₂(teaH₂)₄(O₂CMe)₄][NO₃]₂[O₂CMe]·CH₂Cl₂·MeOH·2H₂O (6**).**

$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.25 g, 1 mmol) was dissolved in 20 ml of MeOH followed by the addition of pivalic acid (0.1 g, 1 mmol) and triethanolamine (0.13 ml, 1 mmol). Triethylamine (0.55 ml, 4 mmol) was then added to produce a deep brown solution which was stirred for 30 min. $\text{Mn}(\text{O}_2\text{CMe})_2 \cdot 4\text{H}_2\text{O}$ (0.25 g, 1 mmol) was subsequently added. The solution was then evaporated to dryness and the residue redissolved in CH_2Cl_2 –MeOH (20 : 2 ml). This was then layered with diethyl ether and brown crystals of **6** appeared after two weeks. Yield: 70 mg, 27.5%. Anal. Calculated (found) for **6**: $\text{Mn}_6\text{C}_{36}\text{H}_{81}\text{O}_{33}\text{N}_6\text{Cl}_2$: C, 28.32 (28.13); H, 5.35 (5.34); N, 5.51 (5.54). Selected IR data ATR (cm^{-1}): 3347br, 1648m, 1577s, 1401m, 1341m, 1160w, 1063w, 1034sh, 901w, 826w, 627w.

Physical measurements

Elemental analyses (CHN) were carried out by Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand. IR spectra were recorded on a Bruker Equinox 55 spectrometer with an ATR sampler provided by Specac Inc. and the samples were run neat.

X-Ray crystallography

X-Ray crystallographic measurements were performed at 123(2) K using a Bruker Smart Apex X8 diffractometer with Mo-K α radiation for samples **2**, **3**, **4** and **5**. The data collection and integration were performed within SMART and SAINT+ software programs, and corrected for absorption using the Bruker SADABS program. X-Ray measurements were performed at 100(2) K for **1** and **6** at the Australian synchrotron MX2 beam-line. The data collection and integration were performed within Blu-Ice¹⁰ and XDS¹¹ software programs. Single crystals were mounted on a glass fibre using oil. **1–6** were solved by direct methods (SHELXS-97), and refined (SHELXL-97) by full least matrix least-squares on all F^2 data.¹² Crystallographic data and refinement parameters for **1–6** are summarized in Table 1. For compounds **1** and **3**, disordered CH_2Cl_2 molecules which could not be modelled satisfactorily were treated by the SQUEEZE program,¹³ which was used to calculate the solvent disorder and remove its overall contribution to the intensity data. The SQUEEZE program was also run for compound **2** due to the large solvent accessible voids present in this structure. Crystallographic details for all compounds are available in the ESI in CIF format.[†]

Magnetic measurements

DC magnetic susceptibility measurements were carried out on a Quantum Design MPMS 5 SQUID magnetometer calibrated by use of a standard palladium sample (Quantum Design) of accurately known magnetization or by use of magnetochemical calibrants such as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Microcrystalline samples were dispersed in Vaseline in order to avoid torquing of the crystallites. The sample mulls were contained in a calibrated gelatine capsule held at the centre of a drinking straw that was fixed at the end of the sample rod. Magnetisation isotherm measurements were made in fields of between 0 and 5 T. AC susceptibilities were made using a Quantum Design PPMS instrument with an AC field of 2 Oe and frequencies varying over the range 10 to 1500 Hz, at temperatures between 2 and 10 K.

Results and Discussion

Synthesis

Initially the dppdH ligand was reacted with the mixed-valent triangular complex $[\text{Mn}_3\text{O}(\text{O}_2\text{CPh})_6(\text{Py})_2(\text{H}_2\text{O})]$ to make a new decanuclear compound $[\text{Mn}_{10}\text{O}_7(\text{dppd})_3(\text{O}_2\text{CPh})_{11}] \cdot 4\text{CH}_2\text{Cl}_2$ (**1**) which displays a novel manganese core topology, with three different oxidation states present – $\text{Mn}_3^{\text{II}}\text{Mn}_6^{\text{III}}\text{Mn}^{\text{IV}}$. In contrast, a simple one pot reaction of $\text{Mn}(\text{BF}_4)_2 \cdot x\text{H}_2\text{O}$ with dppdH in a CH_2Cl_2 –MeOH (10 : 1) solution, layered with hexane led to a Mn^{II} homoleptic cage of the formula $[\text{Mn}_6(\text{dppd})_8][\text{BF}_4]_4$ (**2**). Expanding on this approach by reacting dppdH or pppdH with a Mn^{II} salt, in conjunction with triethanolamine (teaH₃) and in the presence of a suitable base, led to isolation of three iso-structural, divalent heptanuclear complexes of formula $[\text{Mn}_7(\text{pppd})_6(\text{tea})(\text{OH})_3][\text{BF}_4]_2 \cdot 2\text{MeOH} \cdot 2\text{CH}_2\text{Cl}_2$ (**3**). $[\text{Mn}_7(\text{pppd})_6(\text{tea})(\text{OH})_3][\text{NO}_3]_2 \cdot 2\text{MeOH} \cdot 2(\text{CH}_3)_2\text{CO}$ (**3a**). $[\text{Mn}_7(\text{dppd})_6(\text{tea})(\text{OH})_3][\text{BF}_4]_2$ (**3b**). We will describe **3** throughout this paper, the experimental data and crystallographic details for (**3a**) and (**3b**) can be found in the ESI.[†] Note that **3b** formed

Table 1 Crystallographic data for **1**, **2**, **3**, **4**, **5** and **6**

	1	2	3	4	5	6
Formula ^a	Mn ₁₀ C ₁₂₀ H ₉₀ O ₃₅ N ₆ Cl ₈	Mn ₆ C ₁₀₄ H ₇₂ O ₁₆ N ₁₆ B ₄ F ₁₆	Mn ₇ C ₀₄ H ₄₇ N O ₂₀ B ₂ F ₈ Cl ₄	Mn ₇ C ₆₆ H ₉₆ O ₃₀ N ₁₄	Mn ₄ C ₅₂ H ₇₄ O ₂₂ N ₁₂ Cl ₄	Mn ₆ C ₃₆ H ₈₁ O ₃₃ N ₆ Cl ₂
<i>M</i> /g mol ⁻¹	3009.05	2478.65	2334.74	1950.15	1580.79	1526.9
Crystal system	Triclinic	Tetragonal	Triclinic	Cubic	Triclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>I</i> 41	<i>P</i> $\bar{1}$	<i>Pa</i> $\bar{3}$	<i>P</i> $\bar{1}$	<i>Pbcn</i>
<i>a</i> /Å	15.000(3)	29.3102(4)	13.7852(10)	20.4997(2)	9.3709(3)	24.080(5)
<i>b</i> /Å	15.770(3)	29.3102(4)	14.7338(10)	20.4997(2)	12.1927(4)	27.460(6)
<i>c</i> /Å	26.938(5)	15.2712(6)	15.1269(11)	20.4997(2)	15.2722(4)	19.590(4)
α (°)	77.53(3)	90	64.941(3)	90	94.808(10)	90
β (°)	76.12(3)	90	88.285(4)	90	100.43(10)	90
γ (°)	77.04(3)	90	89.973(3)	90	101.778(10)	90
<i>V</i> /Å ³	5939(2)	13119.3(6)	2781.7(3)	8614.75(15)	1666.72(9)	12954(5)
<i>T</i> /K	100(2)	123(2)	123(2)	123(2)	123(2)	100(2)
<i>Z</i>	2	4	1	4	1	8
ρ_{calc} [g cm ⁻³]	1.54	1.255	1.291	1.504	1.575	1.557
λ^b /Å	0.77506	0.71073	0.71073	0.71073	0.71073	0.77056
Data Measured	64555	47271	59886	16454	25884	138066
Ind. reflns	18730	13420	16754	2397	9947	10195
<i>R</i> _{int}	0.0653	0.0691	0.0319	0.0374	0.0334	0.092
Reflns with <i>I</i>	15165	9593	13180	1712	8724	9555
<i>I</i> > 2 σ (<i>I</i>)						
Parameters	1566	652	714	187	432	790
Restraints	163	33	21	33	0	68
<i>R</i> ₁ ^c (obs), <i>wR</i> ₂ ^c (all)	0.0516, 0.130	0.085, 0.245	0.058, 0.176	0.064, 0.20	0.051, 0.123	0.082, 0.229
goodness of fit	1.026	0.965 ^d	1.057	1.049	1.201	1.128
Largest residuals/e Å ⁻³	0.759, -0.825	0.93, -0.93	1.10, -0.814	0.965, -0.773	0.595, -0.75	1.3, -1.65

^a Including solvate molecules. ^b Graphite monochromator. ^c $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$. ^d Flack parameter for **2** is 0.48(3).

weakly diffracting crystals and only yielded a partial structure in which the core is identical to that of **3** and **3a**. Compound **3** is representative of the group and displays a disc like core described below. A third β -diketone, functionalized with an *N*-(2-pyridyl)amino group – paaH, was reacted with Mn(Y)₂·*x*H₂O, Y = NO₃ and ClO₄ to yield two further isostructural Mn^{II} disc like clusters of formula [Mn₇(paa)₆(OMe)₆][NO₃]₂·6MeOH (**4**) and [Mn₇(paa)₆(OMe)₆][ClO₄]₂·4Et₂O·3MeOH·H₂O (**4a**). We will describe **4** throughout this paper, the experimental data and the crystallographic details for (**4a**) can be found in the ESI.† A second reaction of Mn(NO₃)₂·4H₂O with paaH in the presence of triethanolamine yielded a mixed valence, ‘reverse oxidation state’ Mn^{II}Mn^{III} tetranuclear butterfly complex of formula [Mn₄(paa)₄(teaH)₂][NO₃]₂·2MeOH·2CH₂Cl₂ (**5**). Finally a hexanuclear cluster that contains triethanolamine and acetate, of formula [Mn₆O₂(teaH)₄(O₂CMe)₄][NO₃]₂[O₂CMe]·CH₂Cl₂·MeOH·2H₂O (**6**), is isolated which possess the same three oxidation states of Mn, *viz* Mn^{II}Mn^{III}Mn^{IV} found in **1**. First, the known tetranuclear triethanolamine butterfly compound [Mn₄(teaH)₂(teaH)₂(O₃CC(CH₃)₂)₂][O₂C(CH₃)₃]₂ was formed *in situ*, by reacting Mn(NO₃)₂·4H₂O with triethanolamine, pivalic acid and NEt₃. This was then reacted further with Mn(O₂CMe)₂·4H₂O as a source of extra Mn and of bridging acetate ligands, to yield **6**.

Crystal and molecular structures

[Mn₁₀O₇(dppd)₃(O₂CPh)₁₁]₄·4CH₂Cl₂ (**1**). Complex **1** crystallizes in the triclinic space group *P* $\bar{1}$ with the asymmetric unit

containing the cluster and four solvent CH₂Cl₂ molecules. The complex is a decanuclear, mixed-valent manganese compound consisting of three Mn^{II}, six Mn^{III} and one Mn^{IV} ions disposed in the cluster as shown in Fig. 1. The oxidation states of the manganese centres in **1** were determined *via* bond valence sum (BVS) calculations,¹⁴ (Table S1†) coordination geometries and charge balance considerations. The cluster core has a triangular based, layered structure. The top Mn^{III} layer (Mn1–Mn3) consists of a triangular unit bridged by a μ_3 oxide (average Mn···Mn separation of 3.02 Å). This unit resembles the starting triangular benzoate complex, with the μ_3 oxide and surrounding carboxylates still present, three of which have been replaced to allow for further cluster growth. The middle layer consists of four manganese ions – three of which are Mn^{III} ions (Mn5–Mn7) and form a much larger triangle (average Mn···Mn separation of 4.92 Å), while a Mn^{IV} ion (Mn4) lies in the centre of this larger triangle. The bottom layer consists of three Mn^{II} ions (Mn8–Mn10) which forms an intermediate sized triangle (average Mn···Mn separation of 4.29 Å). Overall the positions of the ten metal ions resemble a distorted centred tricapped trigonal prism, with each metal cap (Mn5, Mn6 and Mn7) capping a rectangular face (Fig. 2).

While this core topology has previously been observed in clusters of cobalt and nickel,¹⁵ it has not been seen for large manganese clusters. Furthermore, **1** is the first decanuclear Mn cluster having the oxidation state distribution of Mn^{II}Mn^{III}Mn^{IV}. The cluster appears to be based around the central Mn4 ion which has an octahedral arrangement of six bridging oxides. Three of the oxides are μ_4 bridging, while three are μ_3 and bridge to all other metal ions present in the cluster. The three μ_4 oxides each bridge from Mn4 to two of the Mn sites of the top layer and

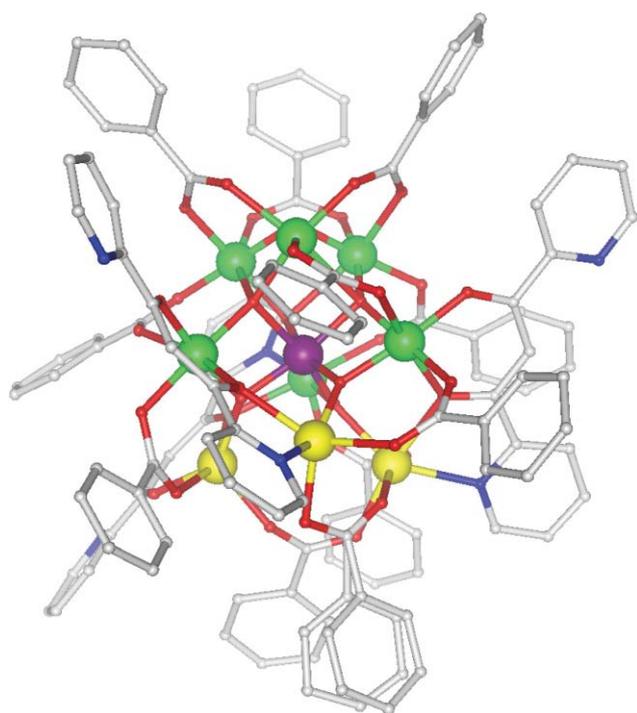


Fig. 1 Weblab viewer representation of **1**, with H atoms omitted for clarity. Mn^{II}, yellow; Mn^{III}, green; Mn^{IV}, purple; O, red; N, blue; C, light grey.

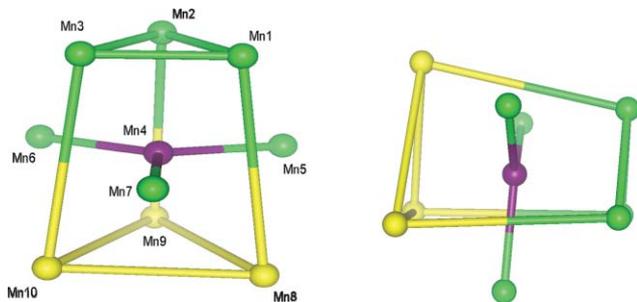
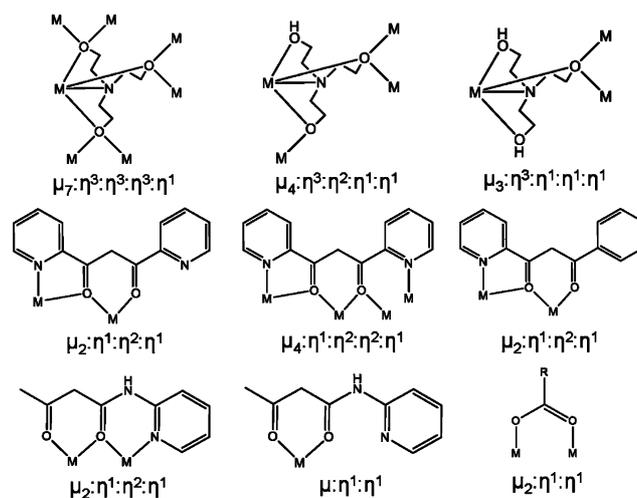


Fig. 2 Weblab viewer representation of the centred tricapped trigonal prismatic core of **1**.

to one of the capping metals. The three μ_3 oxides each bridge from Mn4 to one of the capping metals and to one of the Mn^{II} ions of the bottom layer. The three dppd⁻ ligands that are present all adopt the $\mu_2\cdot\eta^1\cdot\eta^2\cdot\eta^1$ bonding mode, (see Scheme 2, showing the coordination modes of all ligands employed in the script) each bridging the central Mn^{III} triangle to the bottom Mn^{II} triangle through the N- and O-atoms with one of the pyridyl nitrogen atoms being non-coordinated. This is the same type of bonding arrangement that was recently observed by Yang *et al.*,⁵ using the β -diketone ligand containing a single 2-pyridyl group. However, under the present and near identical reaction conditions a different product is isolated. One can only assume that the non-bonding nitrogen atom on the free pyridyl group has a structure determining role when the cluster forms. There are eleven benzoate ligands present that cap the periphery of the cage, all adopting the common *syn, syn, μ* -bridging mode. Two of the Mn^{II} sites Mn8 and Mn10 are five co-ordinate with distorted trigonal bipyramidal and square based pyramidal geometries respectively, while Mn9 is



Scheme 2 Bonding modes displayed by the various forms of triethanolamine (top), dppd⁻, pppd⁻, (middle) paa⁻ and carboxylate ligands (bottom) in compounds **1–6**.

six coordinate with a distorted octahedral geometry. All of the Mn^{III} sites are octahedral and display axially elongated Jahn–Teller distortions. The two axial bonds have an average Mn–O_{ax} bond length of 2.24 Å, while the Mn–O_{eq} and Mn–N_{eq} equatorial bonds have an average bond length of 1.91 Å and 2.06 Å, respectively. The central Mn^{IV} displays octahedral geometry with an average bond length of 1.89 Å. There are no significant intermolecular H-bond interactions between the clusters, however there are some intra- and intermolecular aromatic π stacking interactions between the benzoate and pyridyl rings. The average intramolecular π – π distance between pyridyl and benzoate rings is \sim 3.7 Å. While intermolecular π – π interactions between two adjacent benzoate rings (distance of 3.66 Å) and two adjacent pyridyl rings (distance of 3.48 Å) forms intermolecular π stacked zig-zag chains throughout the crystal (Fig. 3). Bond length ranges for **1** are given in Table 2, while selected bond lengths can be found in the ESI, Table S7.†

[Mn₆(dppd)₈][BF₄]₄ (2**).** Compound **2** crystallizes in the tetragonal space group *I41*. The asymmetric unit contains half the cluster which lies upon an inversion centre, with two tetrafluoroborate counter ions. **2** is a hexanuclear Mn^{II} cluster (Fig. 4) and is a rare example of a homoleptic cluster as it consists of eight bridging dppd⁻ ligands only. Some other homoleptic clusters reported include a [Co₆(chp)₈] (chp = 6-chloro-2-hydroxypyridine) cluster using pyridonate ligands¹⁶ and pentanuclear Mn, Co and Zn clusters using alkoxo-diazine type ligands.¹⁷ **2** is also a rare example of a hexanuclear Mn^{II}-only cluster with the oxidation states of the ions being determined *via* BVS calculations¹⁴ (Table S2†). The core of **2** consists of two triangular units (Mn1a, Mn2, Mn3 and Mn1, Mn2a, Mn3a) which are linked together *via* four μ_2 oxygen atoms derived from the dppd⁻ ligands. The average Mn \cdots Mn distance for each triangle is 3.49 Å and 3.50 Å, respectively. The six manganese sites lie in a near planar arrangement. Topological similarities can be drawn with hexanuclear clusters reported by Dimitrakopoulou *et al.*¹⁸ and Chakov *et al.*¹⁹ which have oxidation state distributions of Mn^{II}₃Mn^{III}₃ and Mn^{II}₆, respectively. In **2** the eight dppd⁻ ligands that stabilize the core adopt two different modes of bonding. Four adopt the $\mu_4\cdot\eta^1\cdot\eta^2\cdot\eta^2\cdot\eta^1$ mode, while four

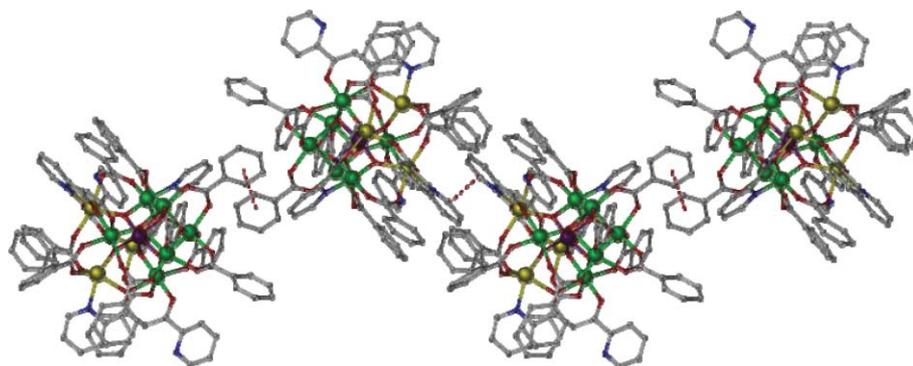


Fig. 3 Intermolecular face-face π - π interactions for **1** (shown as dashed lines).

Table 2 Bond length ranges for **1–6**. (esd's in the range of 2–19)

Atoms for 1	Bond length ranges/Å
Mn(II)–O (trigonal bipyramidal)	2.030–2.196
Mn(II)–N (trigonal bipyramidal)	2.333
Mn(II)–O (octahedral)	2.086–2.278
Mn(II)–N (octahedral)	2.253
Mn(III)–O (octahedral)	1.836–2.432
Mn(III)–N (octahedral)	2.062
Mn(IV)–O (octahedral)	1.852–1.955
Atoms for 2	Bond length ranges/Å
Mn(II)–O (octahedral)	2.174–2.229
Mn(II)–N (octahedral)	2.356–2.406
Mn(II)–O (capped trigonal prism)	2.121–2.317
Mn(III)–N (capped trigonal prism)	2.249–2.309
Atoms for 3	Bond length ranges/Å
Mn(II)–O (octahedral)	2.071–2.237
Mn(II)–N (octahedral)	2.226–2.250
Mn(II)–O (capped trigonal prism)	2.217–2.233
Mn(III)–N (capped trigonal prism)	2.390
Atoms for 4	Bond length ranges/Å
Mn(II)–O (octahedral)	2.091–2.231
Mn(II)–N (octahedral)	2.242
Atoms for 5	Bond length ranges/Å
Mn(II)–O (capped octahedral)	2.1133–2.4524
Mn(II)–N (capped octahedral)	2.333–2.4097
Mn(III)–O (octahedral)	1.8941–2.2251
Atoms for 6	Bond length ranges/Å
Mn(II)–O (capped octahedral)	2.165–2.385
Mn(II)–N (capped octahedral)	2.411–2.446
Mn(III)–O (octahedral)	1.890–2.167
Mn(IV)–O (octahedral)	1.845–1.969

adopt the μ_2 : η^1 : η^2 : η^1 mode. Of the four μ_4 : η^1 : η^2 : η^2 : η^1 ligands present, two lie above and two lie below the plane of the metals.

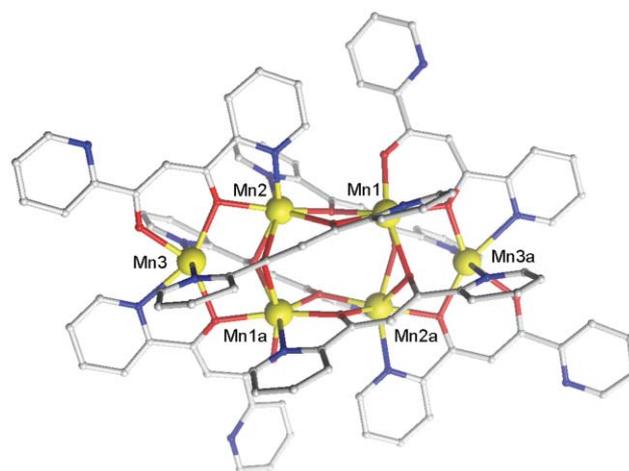


Fig. 4 Weblab viewer representation of **2**, with H atoms omitted for clarity. Mn^{II}, yellow; O, red; N, blue; C, light grey.

Each ligand bridges the two triangular units together through one of the μ_2 O-atoms bonding Mn1 to Mn2 and Mn1a to Mn2a with the pyridyl ring associated to that O-atom chelating. The second μ_2 -O atom of each ligand bridges across the edge of a triangle attaching Mn1a to Mn2 and Mn1 to Mn2a while the pyridyl group bridges to the third metal of the same triangle – Mn3 and Mn3a respectively. There also appears to be weak Mn–O interactions (~ 2.60 Å) between the two μ_2 oxygen atoms that bridge across the edge of each triangle with the third metal site (Mn3 and Mn3a). The four μ_2 : η^1 : η^2 : η^1 dppd[−] ligands each bridge and chelate across the edges of the triangles and lie in the plane of the metals. Mn1, Mn1a, Mn2 and Mn2a are seven-coordinate with distorted, capped trigonal prismatic geometries with average Mn–O and Mn–N distances of 2.22 and 2.28 Å, respectively. Mn3 and Mn3a are six-coordinate with distorted octahedral geometries and with average Mn–O and Mn–N distances of 2.20 and 2.37 Å, respectively. The close proximity of the two oxygen atoms from the dppd[−] towards Mn3 and Mn3a, may suggest that the occupation of a seventh and an eighth coordination site is possible and this would display a distorted square antiprismatic geometry. Compound **2** displays significant intra- and intermolecular π - π interactions. The intramolecular π - π interactions occur between adjacent pyridyl rings of the four dppd[−] ligands that display the μ_4 : η^1 : η^2 : η^2 : η^1 bonding mode (closest face-face aromatic π - π interaction distance of 3.69 Å). The intermolecular π - π interactions

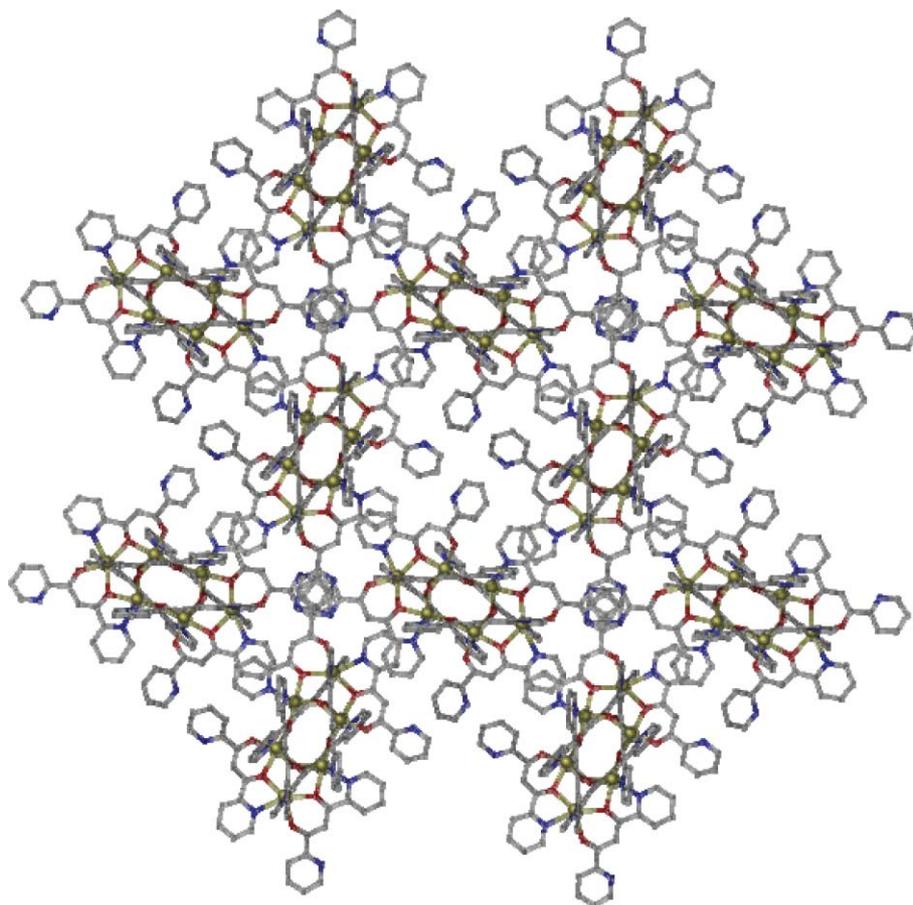


Fig. 5 Nodes of aromatic π - π stacked layers occurring throughout the crystal of **2**.

occur *via* the four dppd^- ligands that display the $\mu_2:\eta^1:\eta^2:\eta^1$ bonding mode. Two of the pyridyl rings of each cluster form 1-D face-face aromatic π stacked layers throughout the crystal (π - π distance 3.85 Å), with four of the other six pyridyl rings interacting with one pyridyl ring of a neighbouring cluster (Fig. 5). Bond length ranges for **2** are given in Table 2, while selected bond lengths can be found in the ESI, Table S8.†

$[\text{Mn}_7(\text{pppd})_6(\text{tea})(\text{OH})_3][\text{BF}_4]_2 \cdot 2\text{MeOH} \cdot 2\text{CH}_2\text{Cl}_2$ (**3**). Complex **3** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit contains half the cluster which lies about an inversion centre, with a tetrafluoroborate counter ion and disordered methanol and CH_2Cl_2 solvent molecules. **3** is a heptanuclear cluster (Fig. 6) in which all the manganese ions are found to be Mn^{II} (Mn1–Mn4 and the symmetry equivalents), assigned using BVS calculations¹⁴ (Table S3†) and charge balance considerations. The metal core of the cluster displays a disc-like topology, that consists of six Mn^{II} sites (Mn2–Mn4 and symmetry equivalents) in a ring surrounding a central Mn^{II} ion (Mn1). This type of topology has been observed on numerous occasions for manganese²⁰ and other transition metals²¹ with various types of bridging ligands. We have observed this type of motif recently, as part of a Mn_{10} compound which was formed when using triethanolamine as a ligand.⁸ Two other compounds related to **3** have also been reported, when using triethanolamine by the Christou²² and Barra²³ groups, both as Mn_7 clusters. In the Mn_{10}

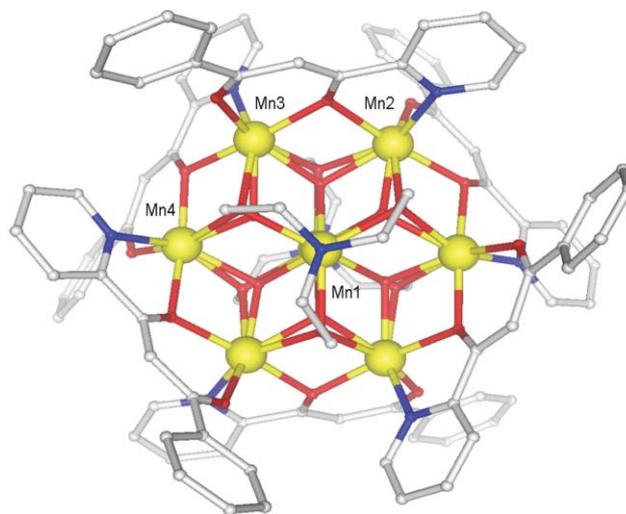


Fig. 6 Weblab viewer representation of **3**, with H atoms omitted for clarity. Mn^{II} , yellow; O, red; N, blue; C, light grey. The central Mn ion (Mn1), the triethanolamine ligand and the three hydroxide ions are disordered over two sites.

case the tea^{3-} lies at the centre of the molecule and is bridging to all of the metal ions of the disc (with three further Mn^{II} atoms attached around the ring).⁸ In the two Mn_7 cases,^{22,23} the triethanolamine ligands are bridging, but lie around the

outside of the disc. What we observe for **3** is the central tea^{3-} case similar to that observed in the Mn_{10} example. Furthermore, in all the cases noted above the oxidation states are mixed-valent $\text{Mn}^{\text{II}}_x\text{Mn}^{\text{III}}_{7-x}$ ions. In **3**, however, only Mn^{II} ions are present, which is unprecedented in this type of cluster. The central tea^{3-} ligand in **3** bridges to the central metal ion and to all six ions of the ring and displays a $\mu_7:\eta^3:\eta^3:\eta^3:\eta^1$ bonding mode. This particular mode of bonding has not been previously observed in triethanolamine cluster chemistry. The presence of three μ_3 hydroxide ions was confirmed *via* BVS calculations, which gave values of 1.1 consistent with the OH^- group. The bridging hydroxides stabilize the metal core bonding from the central ion to two outer ions. Within this central motif the metal, the entire tea^{3-} ligand and the three hydroxide ions are disordered over two sites, with the second positions being generated by an inversion centre. Thus each are at half occupancy. 50% of the time the tea^{3-} lies above the plane of the ring, while 50% of the time the three hydroxides lie below the plane and the other half of the time this is reversed. Overall, this accounts for one metal, one tea^{3-} ligand and three hydroxide ligands. Around the outside of the disc we see six pppd^- ligands, each displaying a $\mu_2:\eta^1:\eta^2:\eta^1$ bonding mode, bridging and chelating to the metal centres, each lying alternatively above and below the plane of the metals. The central metal Mn1 is seven-coordinate displaying capped trigonal prismatic geometry with average Mn–O and Mn–N bond distances of 2.26 and 2.42 Å respectively. The outer Mn sites (Mn2–Mn4 and the symmetry equivalents) all display distorted octahedral geometries, with average Mn–O and Mn–N bond distances of 2.17 and 2.24 Å, respectively. There are some weak intermolecular H-bond interactions between the alpha C–H hydrogen atoms of the β -diketone and the BF_4^- and MeOH solvent molecules. Four of the six C–H's form interactions with four BF_4^- ions, while two of the C–H's interact with the disordered methanol solvent molecules. Each of the four BF_4^- ions are shared between two clusters forming a hexagonal type arrangement of six clusters surrounding one central cluster, {Figure S1 (left)†} with stacked layers above and below {Figure S1 (right)†}. This is also the case for **3a** and **3b** (ESI†). Bond length ranges for **3** are given in Table 2, while selected bond lengths can be found in the ESI, Table S9.†

[Mn₇(paa)₆(OMe)₆][NO₃]₂·6MeOH (4). Compound **4** crystallizes in the cubic space group $P\bar{a}3$ with the asymmetric unit containing two unique manganese sites (Mn1 and Mn2) as well as one paa^- ligand, two methoxides, one nitrate counter ion and a disordered methanol solvent molecule. **4** is a heptanuclear cluster (Fig. 7) consisting of a planar disc-like core similar to that in **3**, with all seven manganese ions again being Mn^{II} as determined by BVS calculations¹⁴ (Table S4†). The planar core of **4** is now stabilized by six μ_3 methoxide ligands, each bridging from the central metal site (Mn2) to two outer ring sites (Mn1 and symmetry equivalents). In the case of **3** the tea^{3-} ligand and three hydroxide ions display a similar type of bridging to the metal ions seen in **4**, the latter has replaced these bridging groups by the six methoxide ligands thus allowing for a similar type of cluster. The six paa^- ligands bond around the edge of the cluster again in a similar manner to the way the pppd^- ligands do in **3** and display the same $\mu_2:\eta^1:\eta^2:\eta^1$ bridging mode. The central metal and outer ring sites are six-coordinate, with octahedral geometries, and with average Mn–O and Mn–N

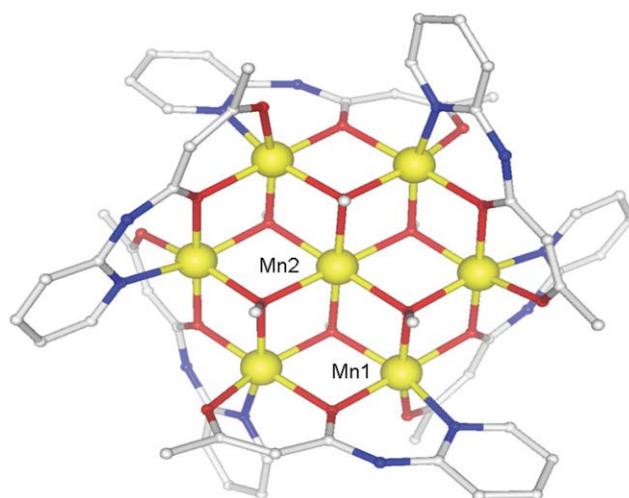


Fig. 7 Weblab viewer representation of **4**, with H atoms omitted for clarity. Mn^{II}, yellow; O, red; N, blue; C, light grey.

bond lengths of 2.19 and 2.24 Å, respectively. This is different to **3** where the central site is seven-coordinate due to the extra bond from the N-atom of the tea^{3-} ligand. The six outer Mn sites in **4** form more regular and less distorted octahedral geometries than in **3**, due to the extra NH chain atom allowing the pyridyl ring to wrap around further, thus lessening the geometric strain. The six NH groups that are present within each cluster form hydrogen bonds to the nitrate counter ions. Each forms a $\text{NH}\cdots\text{O}$ H-bond and thus six nitrates surround each cluster. Each nitrate then forms two further H-bonds to neighbouring clusters, thus the six counter ions are shared between three clusters (Fig. S2†). An extensive 3-D hydrogen bonded network is consequently formed. Interestingly, **4a** displays a different packing mode to **4**, even though the reaction and crystallization conditions used are identical. This is due to the ClO_4^- counter ions being terminally hydrogen bonded to two of the six N–H groups, while solvent Et_2O molecules now present H-bonds to the other four. Alternating layers of clusters and counter ions/solvent molecules occur throughout the crystal of **4a** (Fig. S3†). Bond length ranges for **4** are given in Table 2, while selected bond lengths can be found in the ESI, Table S10.†

[Mn₄(paa)₄(teaH)₂][NO₃]₂·2MeOH·2CH₂Cl₂ (5). Complex **5** (Fig. 8) crystallizes in the triclinic space group $P\bar{1}$ with the asymmetric unit containing half the cluster as well as a nitrate counter ion and CH_2Cl_2 and MeOH solvent molecules. **5** is a mixed-valent tetranuclear cluster consisting of two Mn^{II} and two Mn^{III} ions as deduced from co-ordination geometries and BVS calculations¹⁴ (Table S5†) describing a butterfly topology. This topology and the $\text{Mn}_2^{\text{II}}\text{Mn}_2^{\text{III}}$ oxidation state distribution is common within manganese based cluster chemistry.²⁴ A number of these Mn_4 compounds are known to exist with triethanolamine accompanied by various co-ligands,²⁵ however the choice of co-ligand can appear to dictate the oxidation state distribution within the cluster. The most common case observed is where the Mn^{III} sites adopt the central ‘body’ positions of the butterfly, while the Mn^{II} sites occupy the outer or ‘wingtip’ positions. In the majority of cases reported this has led to an $S = 9$ ground state and with the clusters displaying SMM behaviour.^{25a} This is usually seen when for example carboxylates are used as a co-ligand

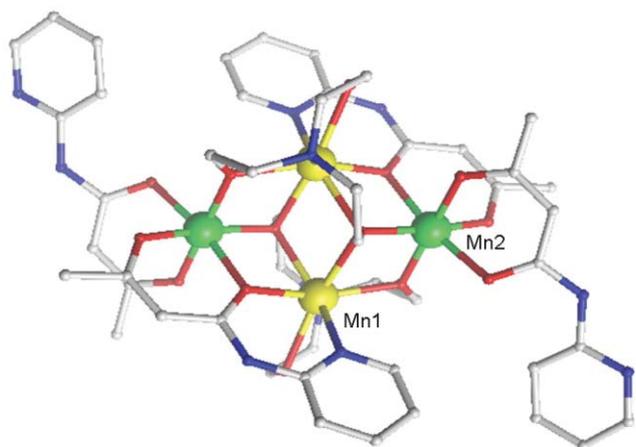


Fig. 8 Weblab viewer representation of **5**, with H atoms omitted for clarity. Mn^{II}, yellow; Mn^{III}, green; O, red; N, blue; C, light grey.

with triethanolamine or when the ligand 2-hydroxymethylpyridine (Hhmp) is used under various conditions.²⁶ The second case and the one observed for **5**, is the reversal of the above mode, such that the Mn^{II} ions are found in the body positions and the Mn^{III} ions as the wingtips. This type of 'reversed' core has only been observed a few times and is rare in manganese cluster chemistry. It was first observed when a β -diketone such as acetylacetonate (acac) was used as a co-ligand in conjunction with triethanolamine, with several other analogues then being isolated.^{25b} In those cases weak anti-ferromagnetic exchange with an $S = 1$ ground state was reported, showing no SMM behavior. The second case reported recently by Brechin *et al.* utilizes the cyclic calix[4]arene ligands in which they report overall weak, but dominant ferromagnetic exchange, with an $S = 7$ ground state.²⁷ This was the first of the reversed oxidation state butterfly clusters to display SMM behaviour. The core of **5** is stabilized by four paa⁻ and two teaH²⁻ ligands. The two teaH²⁻ ligands both adopt the $\mu_4:\eta^3:\eta^2:\eta^1:\eta^1$ bonding mode, bridging to all Mn sites as is the case in other regular and reversed oxidation state butterfly clusters. Two of the four paa⁻ ligands chelate through both oxygen atoms to the wing Mn^{III} ions, with the pyridyl ring non-coordinating. The secondary amine group and the free N-atom of the 'dangling' pyridyl ring are involved in H-bonding to the solvent MeOH molecules and subsequently to neighbouring chelating paa⁻ ligands of adjacent clusters. This produces two intermolecular N...OH...NH bridges forming 1-D chains throughout the crystal (Fig. S3†). The remaining two paa⁻ ligands present bridge the Mn^{II} sites (body) to the Mn^{III} sites (wingtip) *via* the $\mu_2:\eta^2:\eta^1:\eta^1$ bonding mode. The two NH groups here form H-bonds to the two nitrate counter ions, which in turn hydrogen bond to neighbouring clusters through the protonated teaH²⁻ ligands above and below the chain, forming 2-D H-bonded sheets (Fig. 9). The N-(2-pyridinyl) amino substituted β -diketone ligand appears here to play a similar chelating role as in the case of one of the previously reported reverse oxidation state butterfly cluster [Mn₄(teaH)₂(acac)₄(MeOH)₂][ClO₄]₂.^{25b} In **5**, the MeOH molecules in the above mentioned cluster are replaced by chelating N-atoms from the pyridyl ring, with the rest of the ligand backbone being very similar. The two Mn^{II} sites are seven-coordinate with capped octahedral geometries with average Mn–O and Mn–N distances of 2.26 and 2.37 Å respectively, while the two Mn^{III}

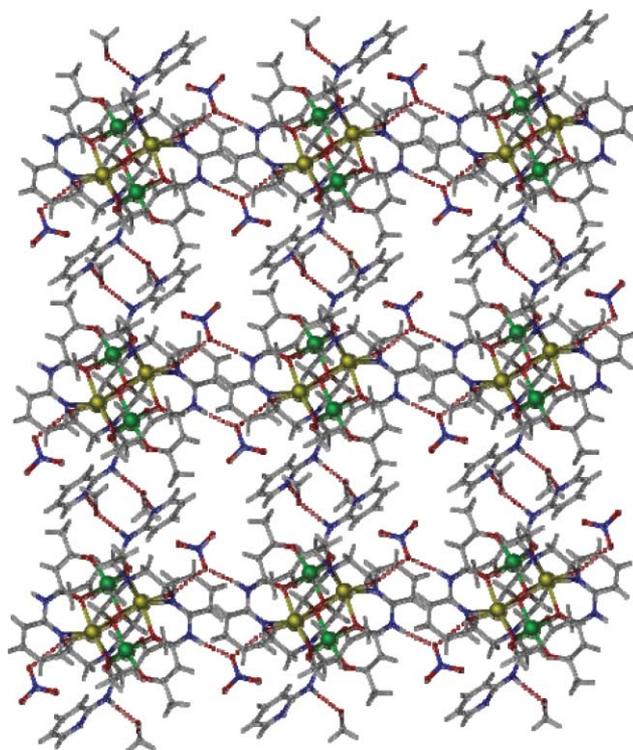


Fig. 9 2-D hydrogen bonding occurring throughout the crystal of **5**.

sites are octahedral and display the usual Jahn–Teller distortions associated with this ion. Average Mn–O_{ax} and Mn–O_{eq} distances are 2.19 and 1.92 Å, respectively. The two axially elongated Jahn–Teller axes in **5** are aligned co-parallel to each other. Bond length ranges for **5** are given in Table 2, while selected bond lengths can be found in the ESI, Table S11.†

[Mn₆O₂(teaH₂)₄(O₂CMe)₄][NO₃]₂[O₂CMe]·CH₂Cl₂·MeOH·2H₂O (**6**). Complex **6** (Fig. 10) crystallizes in the orthorhombic space group *Pbcn* with the asymmetric unit containing the cluster, an acetate and two nitrate counter ions with CH₂Cl₂, MeOH and H₂O solvent molecules. **6** contains three different metal oxidation states, four are Mn^{II} (Mn1, Mn2, Mn5, Mn6), one Mn^{III} (Mn3)

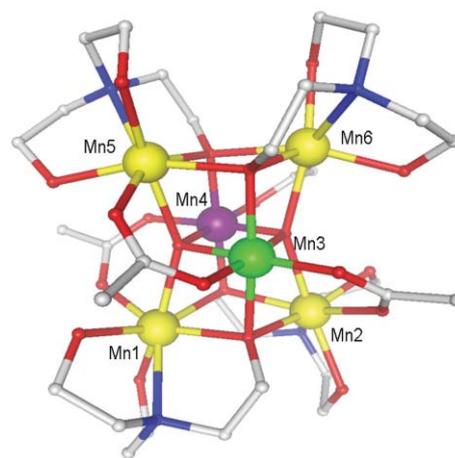


Fig. 10 Weblab viewer representation of **6**, with H atoms omitted for clarity. Mn^{II}, yellow; Mn^{III}, green; Mn^{IV}, purple; O, red; N, blue; C, light grey.

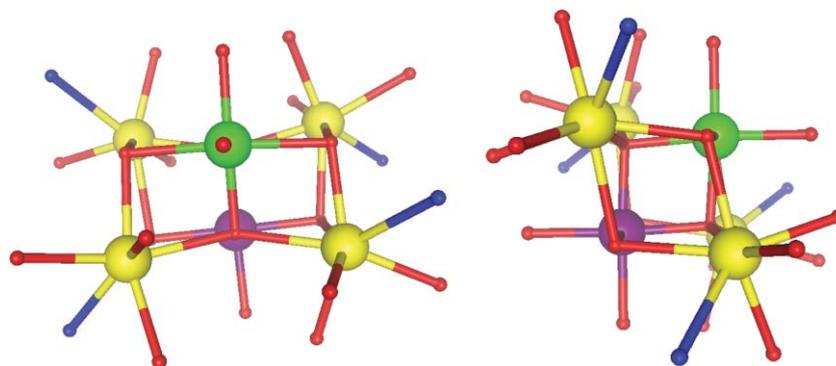


Fig. 11 Weblab viewer representations of the distorted double cubane core of **6**.

and one Mn^{IV} (Mn4). To our knowledge this oxidation state distribution has not been observed previously for a hexanuclear manganese cluster.¹⁸ The oxidation states were determined *via* bond valence sum calculations¹⁴ (Table S6[†]) countered with the coordination geometries of the ions. The core of **6** (Fig. 11) displays a distorted face-sharing double cubane topology made up of six metals and six bridging oxygen atoms. The metal and oxygen sites alternate along the edges of the cubes. The shared face of the cubane contains the Mn^{III} and Mn^{IV} ions that are present within the structure, as well as two μ_4 oxides. The μ_4 oxides are each coordinated to both Mn3 and Mn4 at the corners of the double cubane, as well as to two Mn^{II} ions that complete the outer metal vertices of the two cubes. The remaining four vertices are made up of four μ_3 oxygen atoms derived from the teaH₂⁻ ligands. Mn3 and Mn4 are both octahedrally coordinated with Mn3 containing Jahn–Teller distorted elongated axial bonds with an average Mn–O_{ax} distance of 2.15 Å. The four shorter equatorial bonds have an average Mn–O_{eq} distance of 1.92 Å. Mn4 displays a more regular octahedral environment with average Mn–O distance of 1.92 Å. The four Mn^{II} ions are all seven-coordinate and each have capped octahedral geometries with an average Mn^{II}–L distance of 2.26 Å. The distortion present in the double cubane core is due to the outer Mn^{II} sites which form longer bond lengths and have larger coordination geometries. Selected bond angles within the di-cubanes vary from ~98° between the Mn^{III}–O–Mn^{IV} shared face, up to ~150° along the Mn^{II}–O–Mn^{II} edges. The four triethanolamine ligands that are present are singly deprotonated and each display the $\mu_3:\eta^3:\eta^1:\eta^1:\eta^1$ bonding mode. The nitrogen and the two protonated oxygen atoms of teaH₂⁻ chelate to the Mn^{II} ion while the non-protonated oxygen acts as a μ_3 bridge, bridging to the opposite Mn^{II} site and a face sharing metal site. The four acetate ligands present each bridge across a face of a cube from a Mn^{II} site to either a Mn^{III} or Mn^{IV} ion. There are intermolecular H-bonds formed between the clusters *via* the protonated teaH₂⁻ ligands and the acetate counter ion and these result in 1-D chains. These are then connected *via* the nitrate ions to form 2-D hydrogen bonded sheets (Figure S5[†]). Bond length ranges for **6** are given in Table 2, while selected bond lengths can be found in the ESI, Table S12. [†]This type of face sharing double cubane core has been observed on only three previous occasions in manganese cluster chemistry. The first such compound contained a core of six Mn^{III} ions within the cluster [Mn₆O₄(OMe)₂(O₂CMe)₄(Mesalim)₄] and it was formed by reacting Mn^{II} acetate with methyl salicylimidate in

methanol.²⁸ The core in the Mesalim species and in **6** are stabilized by two μ_4 oxides and both contain four acetate ligands that bridge across the cubane faces. The difference stems from the Mesalim ligand having only one N- and one O- atom involved in bonding thus the four μ_3 bridges are provided by two extra oxides and two methoxides. The Mesalim cluster was found to display a ground state *S* value of 0. The second reported example was of a manganese cluster with oxidation state distribution Mn^{II}₂Mn^{III}₄ encapsulated within a polyoxometalate outer shell and having the general formula {[XW₉O₃₄]₂[Mn₆O₄(H₂O)₄]}¹²⁺.²⁹ In this case the [Mn₆O₆] core was stabilized by two μ_4 and two μ_3 oxides as well as a μ_3 oxygen atom derived from the polyoxometalate. It was found that this cluster had an *S* value of 5 and behaved as a SMM. Finally the third is a recently reported [Mn₆O₄(OMe)₂(O₂CPh)₄(dphmp)₄] (dphmp = diphenyl(pyridine-2-yl)methanol) cluster, which has 6Mn^{III} ions and displays dominant antiferromagnetic interactions with a small ground state of *S* ≈ 3. AC susceptibility measurements however suggest possible SMM behaviour.³⁰

Both **1** and **6** contain three different oxidation states within the same cluster Mn^{II}₃Mn^{III}₂Mn^{IV} for **1** and Mn^{II}₄Mn^{III}₁Mn^{IV} for **6** which is unusual but not uncommon.³¹ The importance of mixed-valent manganese clusters is highlighted by the recent article by Stamatatos and Christou in which they emphasize the different strengths of the exchange interactions within Mn^{II}Mn^{III}, Mn^{III}Mn^{III} and Mn^{III}Mn^{IV} pairs which can lead to situations where Mn^{III}Mn^{IV} interactions, the strongest of the three indicated and which is antiferromagnetic in nature, dominate the coupling interactions in high nuclearity manganese compounds.³² This sometimes leads to molecules having large spin values *S* and, thus, trapped valence clusters of the type Mn^{II}_{*x*}Mn^{III}_{*y*}Mn^{IV}_{*z*} are important in obtaining high spin manganese clusters which may display SMM behavior. In clusters **1** and **6**, however, this did not lead to large spin values as both clusters displayed antiferromagnetic coupling overall (See magnetic data, below) leading to small spin ground states in both cases and no SMM behaviour. Compound **5** is a mixed-valent Mn^{II}₂Mn^{III}₂ compound that utilized paaH and teaH₃ as ligands and leads to a novel reverse oxidation state butterfly cluster. For **2**, **3** and **4** we isolated three new Mn^{II} based clusters. Obtaining all-Mn^{II} clusters is a relatively rare occurrence in manganese cluster chemistry, the syntheses being carried out under basic and aerobic conditions. Only a small number of other homometallic Mn^{II} clusters has been reported, however.³³ There are few such compared to Mn^{II}/Mn^{III} and Mn^{III}

clusters, but this may be due to the goal of ourselves and others in focusing on isolating manganese clusters with (anisotropic) Mn^{III} ions incorporated. Oxidative chemistry has thus been employed in order to isolate higher oxidation Mn compounds, herein containing pyridyl β -diketone ligands.

Magnetic data

DC magnetic susceptibility data were collected on microcrystalline samples of **1**, **2**, **3**, **4**, **5** and **6** in a DC field of 1T, 0.1T and 0.01T, over the temperature range 2–300 K, with the Mn^{III}-containing samples dispersed in a Vaseline mull to prevent torquing of crystallites. Plots of $\chi_M T$ versus T are shown in Fig. 12 for **1**, **2**, **3**, **4** and **6** and Fig. 13 (left) for **5**. The $\chi_M T$ value at 300 K for **1** is 22.5 cm³ K mol⁻¹ which is lower than the value expected for 3Mn^{II}, 6Mn^{III} and 1Mn^{IV} non-interacting ions of 33 cm³ K mol⁻¹ assuming g is close to 2. The $\chi_M T$ value decreases gradually upon lowering the temperature until around 50 K where we observe a much sharper decrease down to 2.94 cm³ K mol⁻¹ at

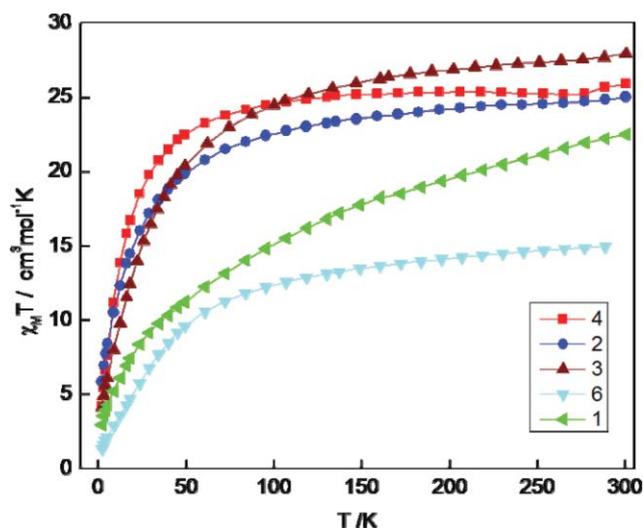
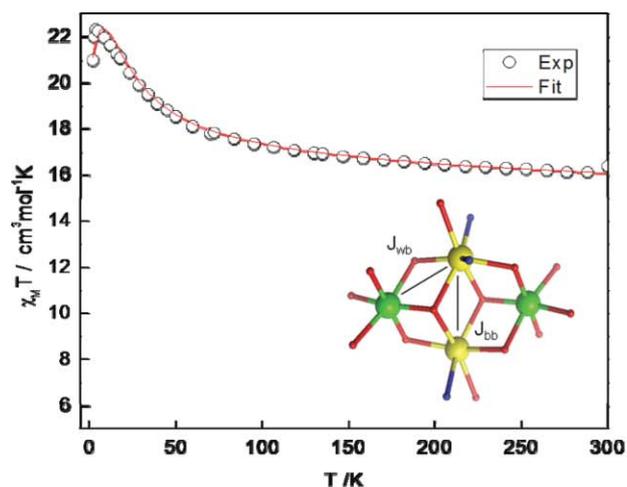


Fig. 12 $\chi_M T$ versus T plots, in a DC field of 1 T for **1**, **2**, **3**, **4** and **6**. The solid lines join up the points.



2 K. This indicates that the dominant intra-cluster interactions are antiferromagnetic in nature with the $\chi_M T$ value indicating a possible ground S value of 2 or 1 for cluster **1**. The S value of 1 is that expected if all spins are aligned antiferromagnetically to each other. The M vs. H isotherms have a pseudolinear dependence without any hint of saturation at 2 K and 5 T, thus indicative of antiferromagnetic coupling (Figure S6[†]), with energy levels likely of greater value but close to that of the ground level. Although the cluster is complex and has many competing magnetic pathways the spin value may be rationalized by looking at three of the Mn^{III}–O–Mn^{III} interactions. The interactions between Mn1–O–Mn7, Mn2–O–Mn5 and Mn3–O–Mn6, each having bonds angle of $\sim 150^\circ$, are likely to produce the strongest antiferromagnetic interactions within the cluster. These pathways will most likely override any Mn^{IV}–O–Mn^{III} interactions and also other competing Mn^{III}–O–Mn^{III} interactions. Together with the Mn^{II} ions being antiferromagnetically coupled to each other, this will lead to the small S value indicated.

Compound **2** has a room temperature $\chi_M T$ value of 25.05 cm³ K mol⁻¹, slightly lower than the value expected for six non-interacting Mn^{II} ions, of 26.25 cm³ K mol⁻¹. This would indicate the presence of weak *anti*-ferromagnetic exchange interactions within the cluster as is commonly observed between Mn^{II} ions. As the temperature is decreased the $\chi_M T$ value steadily decreases down to 50 K whereupon it then decreases more rapidly down to reach 5.85 cm³ K mol⁻¹ at 2 K. The overall shape of the curve confirms dominant antiferromagnetic coupling is occurring within the cluster. The data do not, however, appear to be heading for zero, suggesting a possible non-zero ground spin state. This may be due to the various weak pairwise antiferromagnetic exchange interactions and the Mn₃ triangular topology of the cluster. This will lead to a spin frustration situation, where the spins of the three Mn^{II} ions in the triangle cannot all be antiparallel to each other and, hence, one would expect a non-zero spin ground state. The shapes of the M vs. H isotherms are again indicative of antiferromagnetic coupling, resulting in closely spaced ground levels, the S value of which can not be obtained, unambiguously, from the 2 K/5 T M value (Figure S7[†]). The experimental susceptibility data of **2** were fitted by the MAGPACK program³⁴

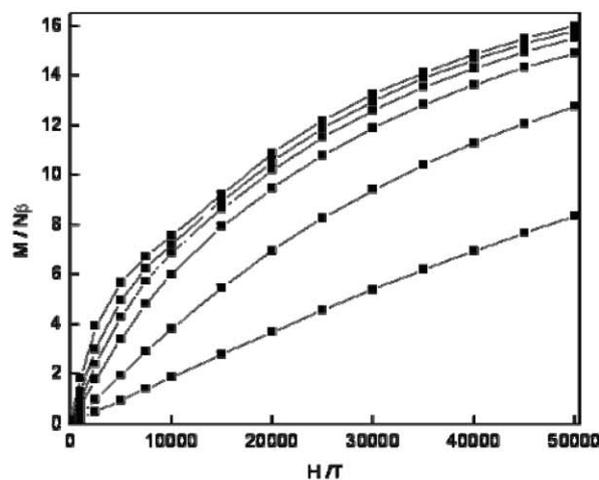


Fig. 13 $\chi_M T$ versus T plot (left) for **5** in a DC field of 0.1 T the solid red line is a fit of the experimental data using the coupling scheme shown inset and M vs. H isothermal plots for **5** (right) in the 2 (top)–20 K (bottom) temperature range, the solid lines are guides for the eye.

using an isotropic three- J model shown in Figure S8 (bottom). ‡This gave best fit parameters of $J_1 = -0.15 \text{ cm}^{-1}$, $J_2 = -1.7 \text{ cm}^{-1}$ and $J_3 = -0.44 \text{ cm}^{-1}$ for $g = 1.99$ {Figure S8 (top)‡}. With these parameters, the spin ground state of the cluster system is not isolated from higher S levels, such that the $S = 0$ to 5 levels all lie within 0.08 cm^{-1} of each other, leading to a quasi-continuum of energy levels. The next closest excited state is the $S = 6$ level which is $\sim 3 \text{ cm}^{-1}$ above the group of ground levels.

Compounds **3** and **4** have the same cluster core and display similar magnetic behaviour. At 300 K, **3** and **4** have $\chi_M T$ values of 27.95 and $25.93 \text{ cm}^3 \text{ K mol}^{-1}$ respectively, values that are a little below that expected for seven non-interacting Mn^{II} $S = 5/2$ ions *viz.* $30.6 \text{ cm}^3 \text{ K mol}^{-1}$, again indicating the presence of weak antiferromagnetic exchange interactions within the clusters. As the temperature is decreased, for **3**, the $\chi_M T$ values decrease slowly down to 50 K whereupon a sharp decrease occurs to reach a value of $4.09 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. For **4**, the value of $\chi_M T$ remains constant between 300 and ~ 50 K suggesting a near total population of all available spin states, again indicating weak exchange with a number of close lying energy levels. The $\chi_M T$ values then start to decrease rapidly below 50 K, to reach $4.21 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. Both plots do not appear to be heading to zero suggesting that a non-zero ground state is possible, the $\chi_M T$ values at 2 K for both **3** and **4** indicating a $S = 5/2$ ground state is likely. This S value, however, cannot be confirmed by the M vs. H isotherm data as each set, even at 2 K, do not saturate and show bigger M values than $5 N\beta$, at 2 K (Fig. S9 and S10‡). The ground states may be rationalized if each outer ring Mn^{II} sites of the disc are aligned antiparallel to each other with the central ion being non-compensated. In attempts to try to quantify the experimental susceptibility data for **3** and **4**, the MAGPACK program³⁴ was again used to find the best fit parameters. Using an isotropic two- J model shown in Fig. S11 (bottom), ‡the best fit parameters for **3** and **4** were found to be $J_1 = -0.1 \text{ cm}^{-1}$ and $J_2 = -0.53 \text{ cm}^{-1}$, for $g = 1.89$, and $J_1 = -0.2 \text{ cm}^{-1}$ and $J_2 = -1.1 \text{ cm}^{-1}$, for $g = 1.95$, respectively {Fig. S11 (top)‡}. These parameter sets are in agreement with the spin ground state of both systems being $S = 5/2$ and with low lying excited states being close in energy, in agreement with the above rationalization.

The $\chi_M T$ values of compound **5**, in a field of 1 T, increase gradually from $16.10 \text{ cm}^3 \text{ K mol}^{-1}$ (300–50 K) up to a maximum of $21.39 \text{ cm}^3 \text{ K mol}^{-1}$ at 12 K before dropping to $8.42 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. **5** displays a small field dependence below 10 K with a maximum $\chi_M T$ value at 0.01 T of $22.66 \text{ cm}^3 \text{ K mol}^{-1}$ which suggests there are low lying excited states close to the ground state (Fig. S12‡). The decrease in $\chi_M T$ observed at very low temperatures may be due to a combination of zero-field splitting and Zeeman thermal depopulation effects. The 300 K value is larger than the spin-only ($g = 2$) of $14.75 \text{ cm}^3 \text{ K mol}^{-1}$ for four non-interacting 2Mn^{II} and 2Mn^{III} high-spin ions, indicating the presence of ferromagnetic interactions. The 2 K value at 0.01 T of $22.66 \text{ cm}^3 \text{ K mol}^{-1}$ suggests a spin ground state is present of at least $S = 6$ (the calculated value for $S = 6$ is $21 \text{ cm}^3 \text{ K mol}^{-1}$ and $S = 7$ is $28 \text{ cm}^3 \text{ K mol}^{-1}$) but the value of $\chi_M T$ will be influenced by zero-field splitting. The M value at 2 K/5 T is not saturated but is close to the $S = 7$ value {Fig. 13 (right)}. The experimental susceptibility data were again fitted by the MAGPACK program³⁴ using the isotropic two- J model shown in Fig. 13 (inset). This gave best fit parameters of $J_{wb} = 5.8 \text{ cm}^{-1}$ and $J_{bb} = -8.7 \text{ cm}^{-1}$ for $g = 2$ (Fig. 13). With these parameters

the spin ground state of the cluster is $S = 6$, with $S = 7$ as the first excited state, 5.8 cm^{-1} above the ground. The data were also fitted using the Heisenberg (Kambe vector coupling) method³⁵ that we have used on other Mn_4 butterfly clusters²⁵ and identical best-fit results were, gratifyingly, obtained when compared to the numerical method inherent in program MAGPACK the latter employing irreducible tensor operator techniques.³⁴ The M vs. H isotherms for **5** were fitted, in the lower field 0–1.5 T range, using the program ANISOFIT 2.0³⁶ and the $S = 6$ spin Hamiltonian $DS_z^2 + E(S_x^2 - S_y^2) + g\beta\mathbf{H}\cdot\mathbf{S}$. The best-fit axial and transverse zero-field splitting parameters were deduced to be $D = -0.31 \text{ cm}^{-1}$ and $E = 0.003 \text{ cm}^{-1}$, respectively, with $g = 2.04$; Fig. 14.

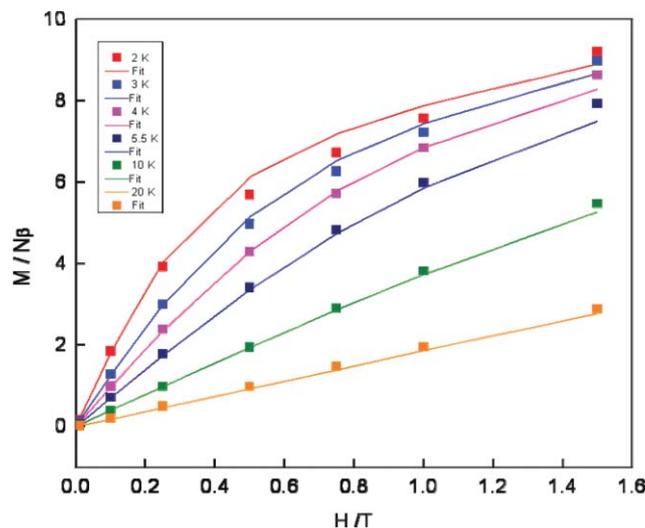


Fig. 14 Observed and calculated magnetization isotherms of **5** in the field range 0–1.5 T. The best-fit parameters for an $S = 6$ state are given in the text.

The D value is similar in size and sign to those obtained on related Mn_4 clusters.²⁵ The magnetization data in the high-field range 1.5 T to 5.0 T did not fit well to the above Hamiltonian because of the effects of close lying excited S levels and their component M_S Zeeman levels.

The magnetism of compound **6** follows a similar pattern to those of compounds **1–4**. The $\chi_M T$ value at 300 K for **6** has a value of $14.95 \text{ cm}^3 \text{ K mol}^{-1}$ which is, again, much lower than the value of the non-interacting value expected for 4Mn^{II} , 1Mn^{III} and 1Mn^{IV} ions of $22.3 \text{ cm}^3 \text{ K mol}^{-1}$, calculated assuming g to be close to 2. This would again indicate dominant antiferromagnetic interactions are occurring within this cluster. The $\chi_M T$ values, shown in Fig. 12, decrease gradually upon lowering the temperature until around 50 K where once more a much sharper decrease occurs, reaching $1.31 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The latter $\chi_M T$ value is close to the $S = 1/2$ value which would be the value expected if all the spins are aligned antiferromagnetically to each other. Again, the shapes of the M vs. H isotherms confirm dominant antiferromagnetic coupling is occurring within the cluster (Fig. S13‡). This small spin ground state may be rationalized, qualitatively, by looking at the five independent magnetic interactions within the cluster (Fig. 12) *viz.* J_1 ($\text{Mn}^{\text{III}}-\text{Mn}^{\text{IV}}$), J_2 ($\text{Mn}^{\text{II}}-\text{Mn}^{\text{II}}$ along the edge of the cube), J_3 ($\text{Mn}^{\text{II}}-\text{Mn}^{\text{II}}$ across the upper and lower faces), J_4 ($\text{Mn}^{\text{III}}-\text{Mn}^{\text{II}}$), J_5 ($\text{Mn}^{\text{IV}}-\text{Mn}^{\text{II}}$). The usual dominant antiferromagnetic coupling between the $\text{Mn}^{\text{III}}-\text{Mn}^{\text{IV}}$ centres J_1 and the likely stronger

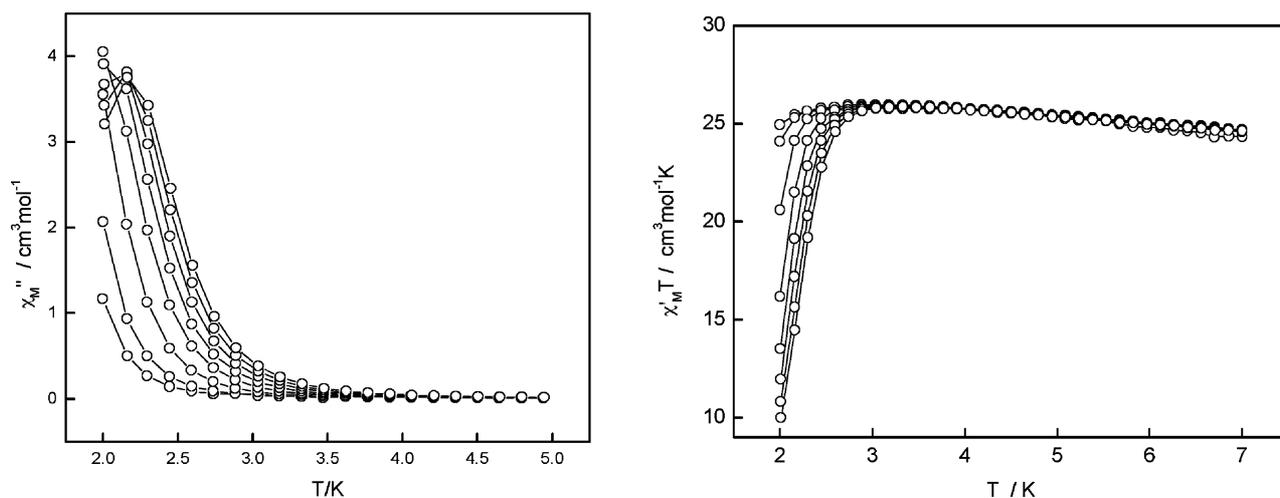


Fig. 15 (right) Plot of χ_M'' vs. T for **5** in AC frequencies 2000 (right), 1500, 1250, 1000, 750, 500, 250, 100 (left) Hz, (left) Plot of $\chi_M'T$ vs. T for **5** using the same frequencies 2000 (bottom)...100 (top) Hz.

coupling between the near linear $\text{Mn}^{\text{II}}\text{--O--Mn}^{\text{II}}$ (151°) centres, J_2 , will cause the edgewise $\text{Mn}^{\text{II}}\text{--Mn}^{\text{II}}$ pairs to have reasonably strong antiferromagnetic J values. These interactions will most likely dominate over the weaker J_3 , J_4 and J_5 values, thus causing the cluster to be antiferromagnetic in nature and the spin ground state to have a likely $S = 1/2$ value. Satisfactory fits for **6** however, could not be obtained due to the complexity of the spin coupling system.

AC magnetic susceptibility data were measured on compounds **1–6** in order to see if there is any slow relaxation of the magnetization. There are no peaks observed in the χ_M'' plots down to 2 K for compounds **1**, **2**, **3**, **4** and **6** indicating that none of these compounds exhibit SMM behaviour, a situation not unexpected for Mn^{II} clusters **2**, **3** and **4**. Compound **5**, however, does display frequency dependent out-of-phase peaks accompanied by collapses in the in-phase signal, thus indicating possible SMM behaviour (Fig. 15). It was only possible to observe a clear maximum in χ_M'' at the highest AC frequency used and thus did not allow us to make an Arrhenius plot in order to deduce the barrier height, U .²⁵ An estimate of U can be obtained from the relation $|DS_z|^2$, which for $S = 6$ yields 17.3 K, a value similar to those found for 'normal oxidation state arrangement' butterfly analogues.²⁵ Cluster **5** is only the second example of a reverse oxidation state butterfly cluster found to behave as a SMM. This observation was to be expected due to the presence of a reasonably large spin ground state and co-parallel Jahn–Teller axes.

The AC measurements, which avoid Zeeman and other effects of the applied DC field, also provide an excellent ancillary tool for the estimation of S . The $\chi_M'T$ value for compound **5** remains relatively constant increasing only very slightly as the temperature is decreased with values of $\sim 24.5 \text{ cm}^3 \text{ K mol}^{-1}$ at 7 K increasing to $\sim 26 \text{ cm}^3 \text{ K mol}^{-1}$ at 3 K. This would suggest there are S values of lower value than the ground state, close in energy, with the $\chi_M'T$ value lying between what is expected for an $S = 6$ or 7 ground state. These data tend to agree with the fit obtained, which has a $S = 6$ as the ground state with a $S = 7$ level 5.8 cm^{-1} away, which is partially populated at low temperatures. The fit also affords $S = 5$ and $S = 4$ as the next closest in energy above these levels, which would account for the slight increase

of $\chi_M'T$ as T decreases. The downward sloping plots of $\chi_M'T$, with decreasing T , observed for **1**, **2**, **3**, **4** and **6** (Fig. S14–S18†), not only mirror the DC $\chi_M T$ data (Fig. 12), as they should, but also indicate that low lying excited states of greater S value than the ground state are being depopulated as T decreases, such that the ground states are not isolated energetically. The population of excited states at these temperatures is a common feature for Mn clusters that have large nuclearities and contain a high percentage of Mn^{II} ions which promotes weak coupling. When dominant antiferromagnetic coupling is observed, then one would expect there to be excited states of higher S values than that of the ground state, and consequent downward sloping plots occurring, as T is decreased. Extrapolating the $\chi_M'T$ signals above 3 K, to avoid decreases due to possible intermolecular effects at low temperatures, to 0 K, gives $\chi_M'T$ values of $\sim 1.2 \text{ cm}^3 \text{ K mol}^{-1}$, $\sim 6 \text{ cm}^3 \text{ K mol}^{-1}$, $\sim 3 \text{ cm}^3 \text{ K mol}^{-1}$, $\sim 4.8 \text{ cm}^3 \text{ K mol}^{-1}$ and $\sim 0.6 \text{ cm}^3 \text{ K mol}^{-1}$ for compounds **1**, **2**, **3**, **4** and **6** respectively. These estimates suggest ground spin values of $S = 1$, 3 , $3/2$ or $5/2$, $5/2$ and $1/2$ for **1**, **2**, **3**, **4** and **6**, respectively. These compare well to those deduced from the DC data and from the fits obtained in some of the cases.

Conclusions

The use of various pyridyl substituted β -diketones such as 1-phenyl-3-(2-pyridyl)propane-1,3-dione (pppdH), 1,3-di(pyridine-2-yl)propane-1,3-dione (dppdH) and N-(2-pyridinyl)acetacetamide (paaH) has yielded several novel clusters and demonstrated that these chelators form a useful class of ligands in manganese cluster chemistry. Compounds **2**, **3** and **4** are rare homovalent Mn^{II} clusters and further attempts to form higher oxidation state clusters with these ligands are presently under way. Triethanolamine has again been successfully introduced into manganese clusters and, in conjunction with paaH, has formed a $\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_2$ tetranuclear butterfly cluster, **5**, with the rare oxidation distribution of two Mn^{II} ions being in the body positions and two Mn^{III} ions at the wingtips. Furthermore, two compounds, **1** and **6**, have been isolated and possess three different Mn oxidation states 'trapped' within each cluster. Fitting of the magnetic susceptibility data to appropriate coupling

models, has yielded J values for most of the clusters (*viz.* **2**, **3**, **4**, **5**) with intra-cluster antiferromagnetic coupling dominant, apart from the case of **5**, for these as well as for compounds **1** and **6**. Cluster **5** shows ferromagnetic (wing-body) and antiferromagnetic (body-body) coupling pathways, with a ground spin state S of 6, close in energy to $S = 7$, and with AC frequency dependent susceptibility data indicative of slow magnetization relaxation and likely SMM behaviour. This is a rare example of a reverse oxidation state $\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_2$ cluster (*vide supra*) displaying SMM features.

Acknowledgements

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