

Unusual Mn_5 cluster with a 'twisted bow-tie' topology and $\text{Mn}^{\text{II}}\text{Mn}_2^{\text{III}}\text{Mn}_2^{\text{IV}}$ oxidation states: Synthesis, structure, and magnetic properties[☆]

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ABSTRACT

The 'reductive aggregation' procedure involving the reaction of MnO_4^- in MeOH in the presence of a carboxylic acid has been extended for the first time to the use of a dicarboxylic acid and the additional presence of a chelate, namely phthalic acid (phthH_2) and 2,2'-bipyridine (bpy), respectively. The MnO_4^- : phthH_2 :bpy = 1:2:1 reaction in MeOH has led to isolation of $[\text{Mn}_5\text{O}_4(\text{phth})_3(\text{phthH})(\text{bpy})_4](\text{phthH}_2)(\text{phthH})$ (**1**), whose Mn_5 cation possesses a 'twisted bow-tie' topology comprising two near-perpendicular $\text{Mn}_3^{\text{II,III,IV}}$ scalene triangles fused at the Mn^{II} ion. Each triangle is bridged by a central $\mu_3\text{-O}^{2-}$ and a $\mu_2\text{-O}^{2-}$ on the $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ edge. Peripheral ligation is provided by the phthalate groups bridging in various modes, and a chelating bpy on each Mn^{III} and Mn^{IV} ion. The cation is a rare example of a cluster with three Mn oxidation states, and it is also the first Mn^{IV} -containing phthalate complex. Fitting of variable-temperature, solid-state dc magnetic susceptibility data collected in a 0.1 T field in the 5.0–300 K range gave $J_1 = J(\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}) = -116(3) \text{ cm}^{-1}$, $J_2 = J(\text{Mn}^{\text{II}}\text{Mn}^{\text{IV}}) = -6.0(4) \text{ cm}^{-1}$, $J_3 = J(\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}) = +3.8(8) \text{ cm}^{-1}$, and $g = 1.95$, with $\text{TIP} = 500 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. These indicate an $S = 7/2$ spin ground state, which was confirmed by a fit of magnetization data collected in the 0.1–7.0 T and 1.8–10.0 K ranges, and by ac in-phase susceptibility data in zero dc field and a 3.5 G ac field at a 1000 Hz frequency.

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1. Introduction

One of our major objectives during the many years that we have been interested in molecular 3d, 3d/4f, and 3d/main group M/O cluster chemistry has been the development of new synthetic procedures that could lead to new metal nuclearities, new structures, and new properties. For various reasons, we have concentrated much of our effort in Mn/O chemistry with primarily carboxylate and/or other O-based ligation. One such reason has been the desire to model the mainly carboxylate ligated Mn_4Ca unit of the photosynthetic oxygen-evolving complex (OEC) in green plants and cyanobacteria [1], and we have introduced multiple generations of Mn_4 and Mn/Ca model complexes over the years [2,3]. Another stimulus for us and other groups was the discovery within Mn chemistry of the new phenomenon of single-molecule magnets (SMMs), and other interesting magnetic clusters in general, with a truly dazzling array of homo- and heterometallic Mn clusters being subsequently discovered, with the highest nuclearity

continuing to be the giant Mn_{70} and Mn_{84} SMMs with a torus structure [4–9].

The synthetic procedures to Mn/O clusters have spanned a wide range, including oxidation of Mn^{II} reagents by atmospheric O_2 , comproportionation of Mn^{II} and MnO_4^- , treatment of preformed clusters with various chelates also capable of bridging, and others [9–15]. One new procedure that we introduced many years ago is what we named 'reductive aggregation', involving the reduction and methanolysis of MnO_4^- in MeOH containing a carboxylic acid, triggering aggregation [9,16,17]. The MeOH has a multiple function as solvent, reducing agent, and potential source of MeO^- ligands, and this convenient single-source procedure has proven to be a rich source of high oxidation state $\text{Mn}^{\text{III/IV}}$ polynuclear products. The identity of the product has been found sensitive to the nature of the carboxylic acid employed, i.e. factors such as bulkiness, aromatic vs aliphatic, etc., reflecting their influence on the undoubtedly complicated, multi-step cluster assembly, and leading to a range of $\text{Mn}_x\text{O}/\text{OMe}/\text{O}_2\text{CR}$ clusters being obtained over the years [9,16,17]. Most of these were also new SMMs, and some possessed fascinating Mn_x structures, such as the Mn_{16} clusters with near-planar grid [16] or W-shaped [17] topologies.

With the homometallic chemistry providing a firm foundation, the reductive aggregation procedure was more recently extended

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to heterometallic Mn/Ce chemistry, leading to the synthesis of a number of Mn/Ce/O/OMe/O₂CR clusters with interesting properties and showing again that new structural types could be obtained that were not available from other approaches [18]. The present work represents a further extension of the procedure to more complicated systems, namely where the carboxylic acid has been replaced with a dicarboxylic acid. As part of this, we have also initiated adding a chelate ligand to preclude the formation of polymers that often plague the use of dicarboxylic acids alone. We now report the initial success of our new thrust, the preparation of a pentanuclear cluster from the use in reductive aggregation of phthalic acid (phthH₂; benzene-1,2-dicarboxylic acid) and 2,2'-bipyridine, and describe the synthesis, crystal structure, and magnetic properties of mixed-valence [Mn₅O₄(phth)₃(phthH)(bpy)₄](phthH₂)(phthH) (**1**; Mn^{II}, 2Mn^{III}, 2Mn^{IV}) with a 'twisted bow-tie' topology.

2. Experimental

2.1. Synthesis

All manipulations were performed under aerobic conditions using chemicals as received, unless otherwise stated. NⁿBu₄MnO₄ was prepared as described elsewhere [19]; phthH₂ = phthalic acid, bpy = 2, 2'-bipyridine.

2.1.1. [Mn₅O₄(phth)₃(phthH)(bpy)₄](phthH₂)(phthH) (**1**)

To a stirred solution of phthH₂ (0.46 g, 2.76 mmol) and bpy (0.22 g, 1.38 mmol) in MeOH (7.5 ml) was added solid NⁿBu₄MnO₄ (0.50 g, 1.38 mmol) in small portions, resulting in a dark purple solution that quickly turned dark brown. After an additional five minutes of stirring, the solution was filtered and the filtrate left undisturbed at ambient temperature for 1 week, during which time slowly grew black crystals of **1**·11MeOH. The crystals were maintained in the mother liquor for X-ray crystallography, or collected by filtration, washed with MeOH, and dried *in vacuo*. The yield was typically 15–20%. Vacuum-dried material analyzed as **1**·³/₂H₂O. Anal. Calc (Found) for **1**·³/₂H₂O (C₈₈H₆₃Mn₅N₈O_{29.5}): C, 53.40 (53.60); H, 3.21 (3.14); N, 5.66 (5.21) %. Selected IR data (KBr, cm⁻¹): 3415(w), 3053(m), 1606(s), 1585(s), 1563(s), 1473(m), 1446(m), 1393(s), 1344 (s), 1315(m), 1147(w), 1107(w), 1085(w), 1058(w), 1035(w), 867 (w), 770(s), 728(m), 713(w), 656(m), 600(s), 501(m), 460(m).

2.2. X-ray crystallography

A suitable single crystal of **1**·11MeOH was attached to a glass fiber using silicone grease and transferred to the goniostat where it was cooled to 100 K for characterization and data collection using MoK_α radiation (λ = 0.71073 Å) on a Bruker Dual micro source D8 Venture diffractometer and PHOTON III area detector running the APEX3 software package. The data frames were integrated and multi-scan scaling was applied in APEX3. Intrinsic phasing structure solution provided all of the non-H atoms. The structure was refined on F² in SHELXL2015 using full-matrix least-squares cycles [20]. The non-H atoms were refined with anisotropic thermal parameters, and all H atoms except H14 were placed in calculated idealized positions and refined riding on their parent atoms. H14, which is involved in the intra-cation O14–H14··O11 hydrogen-bond between the phthalic acid ligand and a phthalate ligand, was sought and located in a difference Fourier map and refined freely.

The asymmetric unit contains the complete Mn₅ cluster cation, parts of two close phthH_x that provide the counter-anion (*vide infra*), and eleven molecules of MeOH. The anion pair and solvent molecules were too disordered to be modeled properly, thus

program SQUEEZE [21], a part of the PLATON package of crystallographic software, was used to calculate the anion and solvent disorder area and remove its contribution to the overall intensity data. Most of the aromatic rings in the cation are also disordered and were refined in two parts. From the structural parameters and the metric parameters at the Mn centers we concluded that the cluster carries a +1 charge. As a result, we assign the two close disordered phthH_x as a phthH₂/phthH⁻ hydrogen-bonded –1 counter-anion. In the final cycle of refinement, 23,016 reflections (of which 18,293 are observed with I > 2σ(I)) were used to refine 908 parameters and the resulting R₁, wR₂ and S (goodness of fit) were 3.85%, 9.69% and 1.068, respectively. The refinement was carried out by minimizing the wR₂ function using F² rather than F values. R₁ is calculated to provide a reference to the conventional R value but its function is not minimized (Table 1).

2.3. Physical measurements

Infrared spectra were recorded on crushed polycrystalline samples as KBr pellets on a Nicolet Nexus 670 FTIR spectrometer in the 400–4000 cm⁻¹ range. Elemental analyses (C, H and N) were performed by Atlantic Microlab in Norcross, Georgia, USA. Variable-temperature dc and ac magnetic susceptibility data were collected using a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 Tesla magnet and operating in the 1.8–300 K range. Samples were embedded in solid eicosane to prevent torquing. Magnetization vs. field and temperature data were fit using the program MAGNET [22a], and D vs g fit error surfaces were generated using the program GRID [22b]. Pascal's constants were used to estimate the diamagnetic correction [23], and contributions from the eicosane and gel capsule were measured as a blank. All these were subtracted from the experimental susceptibility to give the molar paramagnetic susceptibility (χ_M). Ac magnetic susceptibility measurements were carried out on a microcrystalline vacuum-dried sample in the 1.8–15.0 K range using a 3.5 G ac field with a 1000 Hz oscillation frequency.

3. Results and discussion

3.1. Synthesis

The simplicity of the reductive aggregation procedure as a route to high oxidation state Mn/O clusters makes it readily amenable to

Table 1
Crystallographic and structure refinement data for **1**·11MeOH.

	1 ·11MeOH
Formula	C ₉₉ H ₁₀₄ Mn ₅ N ₈ O ₃₉
FW (g mol ⁻¹) ^a	2304.60
Space group	C2/c
a (Å)	35.735(3)
b (Å)	23.5362(17)
c (Å)	25.4197(18)
β (°)	110.249(2)
V (Å ³)	20058(3)
Z	8
T (K)	100(2)
λ (Å)	0.71073
ρ _{calc} (g cm ⁻³)	1.526
R ₁ ^b , c	0.0385
wR ₂ ^{b,d}	0.0969

^a Including solvent molecules.

^b I > 2σ(I).

^c R₁ = Σ(|F_o| - |F_c|) / Σ|F_o|.

^d wR₂ = [Σ[w(F_o² - F_c²)²] / Σ[w(F_o²)²]]^{1/2}, w = 1/[σ²(F_o²) + (m*²) + n*p], p = [max(F_o², 0) + 2*F_c²]/3, m and n are constants.

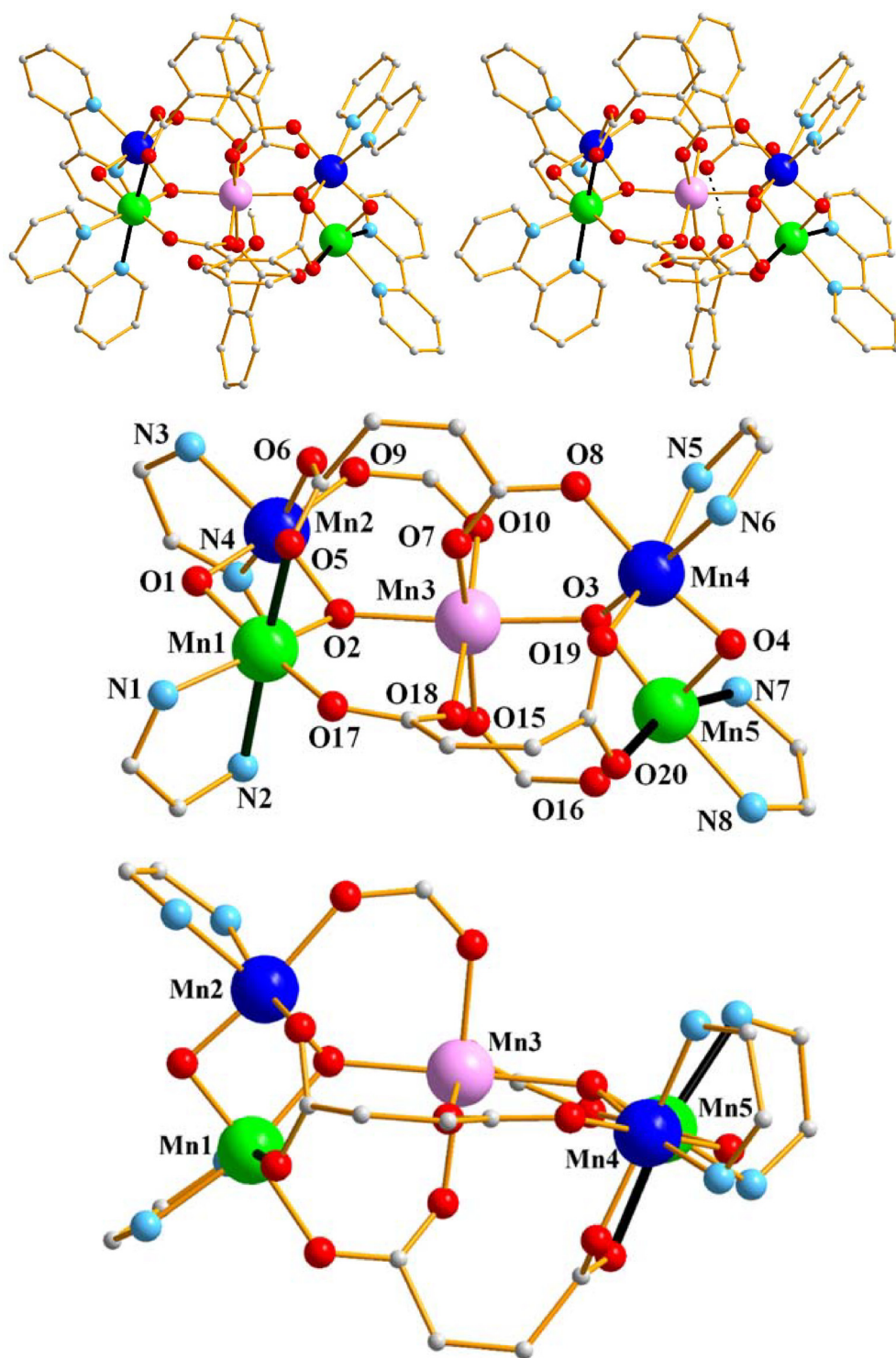
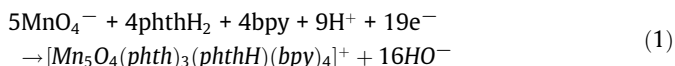


Fig. 1. (top) a stereopair of the complete cation of 1, with the intra-cation O14-H14...O11 hydrogen-bond indicated by the dashed line; (middle) a labeled simplified representation; and (bottom) its core from a viewpoint that emphasizes the near-perpendicular arrangement of the two Mn^{II}Mn^{III}Mn^{IV} triangles fused at the central Mn^{II} (Mn3). H atoms have been omitted for clarity. Thicker bonds in black denote Jahn-Teller elongation axes. Color code: Mn^{IV} blue; Mn^{III} green; Mn^{II} violet; O red; N sky blue; C grey. ((Color online.))

variation in the carboxylic acid employed and the addition of a chelate. The only proviso is that easily oxidized reagents should be avoided. We have thus initiated studies of dicarboxylic acids

with 2,2'-bipyridine as an oxidation-resistant chelate, and report here our initial success with phthalic acid (phthH₂). With the increased number of reagents, more permutations of reaction

ratios are possible, and a variety of the latter have been explored in reaching the procedure described. Thus, the reaction of $N^B\text{Bu}_4\text{-MnO}_4$, phthH_2 , and bpy in a 1:2:1 molar ratio in MeOH gave a dark brown solution and subsequent isolation of **1**·11 MeOH . Its formation is summarized in Eq. (1), but the low yield (typically 15–20%) no doubt reflects a



complicated system possibly with additional products such as dinuclear $[\text{Mn}_2\text{O}_2(\text{O}_2\text{CR})\text{X}_2(\text{bpy})_2]^{n+}$ (X = solvent, Cl^- , etc) species common with bpy [24], but we were unable to successfully isolate any other pure species from the still-colored filtrate. In the absence of bpy , the reaction color bleaches to essentially colorless, indicating reduction of the MnO_4^- all the way to Mn^{II} products, which were not pursued given the many Mn^{II} /phthalate compounds already known [25]. When the concentration of MnO_4^- was halved or doubled, the same Mn_5 product **1** was isolated in comparable and slightly lower yields, respectively. Small changes to the amount of phthH_2 also gave **1**, but decreasing it significantly gave an insoluble brown precipitate – this is not surprising since one of the functions of the acid is to prevent MnO_2 formation. Attempts to obtain simpler salts of the cation by addition of ClO_4^- to the reaction were unsuccessful. The analogous reaction can be performed in EtOH to give an isostructural Mn_5 cluster, but the crystal quality was not as consistent. When the bpy was absent or replaced by pyridine, 2-hydroxymethylpyridine, methyldiethanolamine, 1,1,1-tris(hydroxymethyl)ethane, or 1,8-hydroxyquinoline, it did not prove possible to isolate clean products from the reaction solutions. A similar result was obtained when the two equivalents of phthalic acid in the reaction were substituted by acetic acid, propionic acid, benzoic acid, salicylic acid, succinic acid, phenylmalonic acid, or phenylsuccinic acid.

3.2. Description of structure

A stereopair of the complete Mn_5 cation of **1** and its labeled central portion are shown in Fig. 1. Selected interatomic distances and angles are listed in Table 2. 1·11 MeOH crystallizes in monoclinic space group C2/c with the Mn_5 cation in a general position. Its $[\text{Mn}_5(\mu_3\text{-O})_2(\mu\text{-O})_2]^{8+}$ core comprises two triangular $\{\text{Mn}^{\text{III}}, \text{IV}_3(\mu_3\text{-O})\}$ units fused at the central Mn^{II} atom, Mn3 , and near-perpendicular (angle between Mn_3 planes = 80.26°) to give a ‘twisted-bow-tie’ topology, with an additional $\mu_2\text{-O}^{2-}$ ion bridging the Mn^{III} - Mn^{IV} edges at each end. All five Mn ions are six-coordinate with

near-octahedral geometry, and their assigned oxidation states were established by charge considerations, bond valence sum (BVS) calculations (Table 3) [26], and the clear Jahn-Teller (JT) distortions of Mn^{III} ions Mn1 and Mn5 . These take the form of axial elongations, with the elongated Mn^{III} -O bonds ($2.213(2)$ – $2.228(2)$ Å) and Mn^{III} -N bonds ($2.215(2)$ – $2.239(4)$ Å) being at least 0.1 – 0.2 Å longer than the other Mn^{III} -O bonds ($1.839(2)$ – $1.980(2)$ Å) and Mn^{III} -N bonds ($2.086(2)$ – $2.111(3)$ Å). Each JT axis is near-perpendicular to its Mn_3 plane and thus also to each other [Fig. 1]. The phth^{2-} and phthH^- ligands provide a variety of additional bridges between the metal ions: (i) for two phth^{2-} ligands, one of their carboxylate groups bridges a $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ pair at one end of the cation and the other bridges the central Mn^{II} with a Mn^{III} or Mn^{IV} at the other end; (ii) the third phth^{2-} ligand bridges a $\text{Mn}^{\text{II}}\text{Mn}^{\text{IV}}$ pair (Mn2Mn3) with one carboxylate and its other one remains unbound; and (iii) the phthH^- ligand bridges a $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ pair (Mn3Mn5) with its deprotonated carboxylate, while its protonated acid group remains unbound and hydrogen-bonded to the unbound carboxylate group of the third phth^{2-} ($\text{O14-H14}\cdots\text{O11}$) with $\text{O14}\cdots\text{O11} = 2.538(4)$ Å. Peripheral ligation in the cation is then completed by a bpy chelate on each Mn^{III} and Mn^{IV} . The protonated acid group is supported by the O BVS calculations, which give values of 1.39 and 1.28 for O11 and O14 , respectively (Table 3), indicating them to be sharing an H^+ [26,27]. In addition to the Mn_5 cation, two molecules of ‘phthalate’ and approximately eleven MeOH molecules were observed in the asymmetric unit but they were too disordered to be refined. The former are thus assigned as a $\text{phthH}_2/\text{phthH}^-$ hydrogen-bonded anion pair giving charge-balance with the $\text{Mn}_5 + 1$ cation. The BVS values of the $\mu_2\text{-O}^{2-}$ ions O1 and O4 at each end of the cation are 1.65 and 1.59, respectively, lower than expected for oxides, which we assign to their involvement in hydrogen bonding with disordered solvent MeOH molecules.

The complete cation can alternatively be described as two $[\text{Mn}_2^{\text{III,IV}}(\mu_2\text{-O})_2(\text{O}_2\text{CR})(\text{bpy})_2\text{X}_2]^{2+}$ (X = H_2O or similar) units, which are well known in dinuclear Mn/O chemistry [28], being linked by a Mn^{II} attaching to one of their O^{2-} ions making them μ_3 (Fig. 1), and their RCO_2^- becoming a phth^{2-} and bridging to the Mn^{II} and the other Mn_2 unit at its X site. Examination of the packing shows that the cation forms π -stacked dimers involving phth^{2-} ligands on neighboring Mn_5 cations, with an inter-ring distance of 3.385 Å (Fig. 2). In addition, there are a number of weaker inter-cation bpy/bpy interactions giving a 3D network.

The cation of **1** is thus at the $\text{Mn}_2^{\text{IV}}/\text{Mn}_2^{\text{III}}/\text{Mn}^{\text{II}}$ oxidation level. Three Mn oxidation states in the same cluster is rare but not unprecedented, having been seen previously, for example, in Mn_9 , Mn_{25} , and Mn_{30} complexes, as well as the reduced forms, $[\text{Mn}_{12}\text{O}_{12}]^{2-}$

Table 2
Selected interatomic distances (Å) and angles ($^\circ$) for **1**·11 MeOH .

Mn1-N1	2.0859(19)	Mn3-O10	2.1373(15)
Mn1-N2	2.2151(19)	Mn3-O15	2.1214(15)
Mn1-O1	1.8393(15)	Mn3-O18	2.1712(15)
Mn1-O2	1.8909(13)	Mn4-O3	1.8027(16)
Mn1-O5	2.2282(15)	Mn4-O4	1.8075(17)
Mn1-O17	1.9798(15)	Mn4-O8	2.0029(16)
Mn2-O1	1.7902(14)	Mn4-O19	1.9387(16)
Mn2-O2	1.8021(14)	Mn4-N5	2.080(7)
Mn2-O6	1.9182(14)	Mn4-N6	2.026(15)
Mn2-O9	1.9771(13)	Mn5-O3	1.8852(15)
Mn2-N3	2.0619(18)	Mn5-O4	1.8268(18)
Mn2-N4	2.0357(17)	Mn5-O16	1.9626(17)
Mn3-O2	2.1237(14)	Mn5-O20	2.2127(17)
Mn3-O3	2.1213(15)	Mn5-N7	2.239(4)
Mn3-O7	2.1061(15)	Mn5-N8	2.111(3)
Mn1-O1-Mn2	95.50(7)	Mn3-O3-Mn4	126.26(7)
Mn1-O2-Mn2	93.33(6)	Mn4-O3-Mn5	94.49(7)
Mn2-O2-Mn3	128.70(7)	Mn3-O3-Mn5	125.84(8)
Mn1-O2-Mn3	126.60(7)	Mn4-O4-Mn5	95.65(8)

Table 3
BVS values and assignments for Mn and selected O atoms in **1**·11 MeOH .

Atom	Mn^{II}	Mn^{III}	Mn^{IV}
Mn1	3.27	3.04	3.12
Mn2	4.23	3.93	4.03
Mn3	2.24	2.15	2.15
Mn4	4.10	3.81	3.90
Mn5	3.25	3.02	3.09
Atom	BVS Assignment		
O1	1.65	O^{2-}	
O2	1.90	O^{2-}	
O3	1.91	O^{2-}	
O4	1.59	O^{2-}	
O11	1.39	RCO_2H	
O14	1.28	RCO_2H	

^a For Mn , the metal oxidation state is the nearest integer to the bold underlined value, which is the closest to the charge for which it was calculated. For O, values in the ~ 1.8 – 2.0 , ~ 1.0 – 1.2 , and ~ 0.2 – 0.4 ranges indicate non-, single- and double-protonation, respectively, but can be affected by hydrogen-bonding.

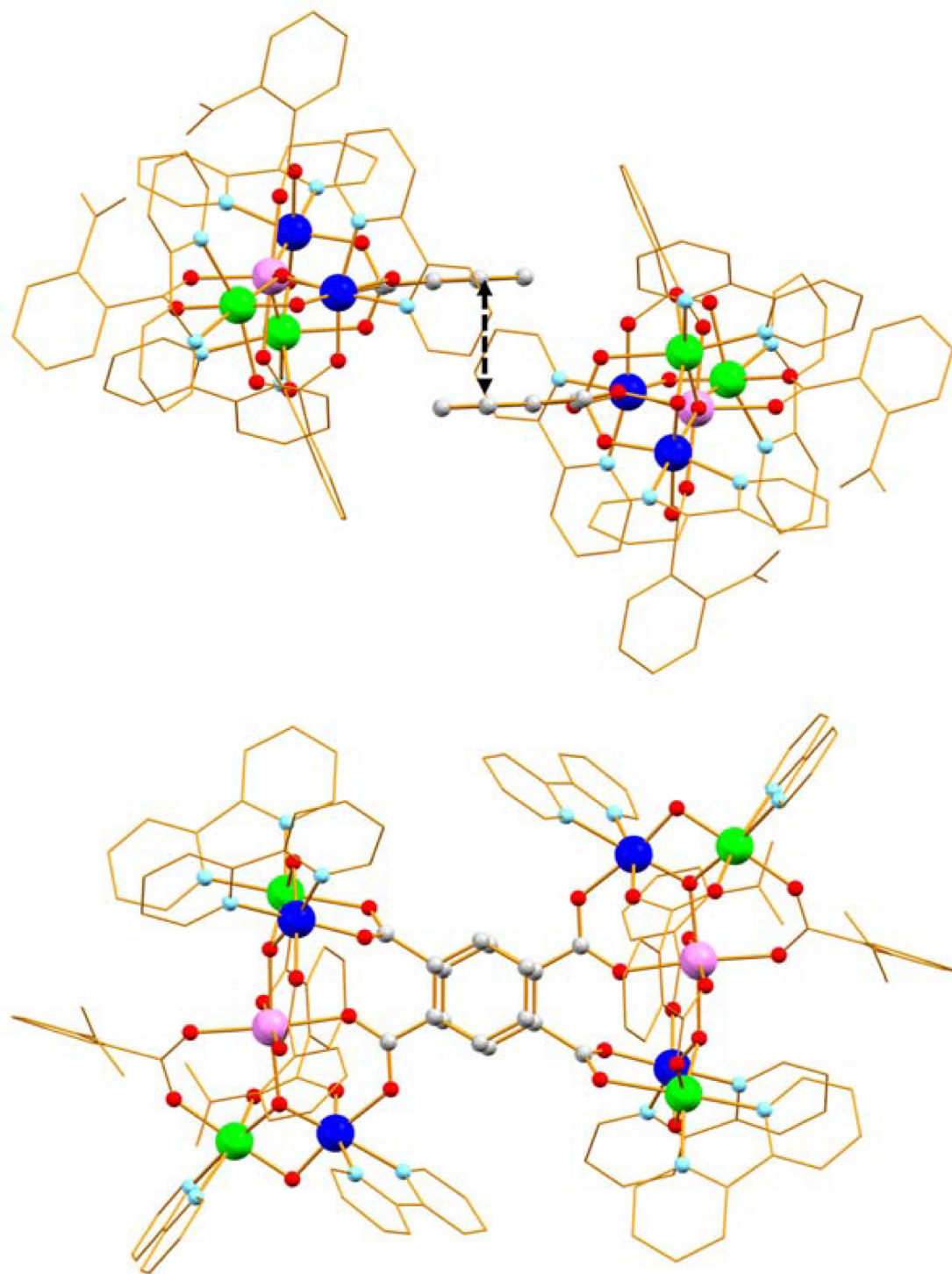


Fig. 2. The π - π stacking between phthalate Ph rings on adjacent molecules of the cation of **1** viewed (**top**) from the side, and (**bottom**) from the top. The distance between the two rings is 3.39 Å. Color code: Mn^{IV}, blue; Mn^{III}, green; Mn^{II}, violet; O, red; N, sky blue; C, grey; black dashed line to indicate the separation between the stacked rings. ((Color online.))

Table 4Structural types and ground state S values for Mn₅ Clusters.

Complex ^{a,b}	Oxid. States	Mn ₅ Topology	S	Ref.
[Mn ₅ (OH) ₂ (trazH) ₂ (SO ₄) ₄]	5Mn ^{II}	Edge-sharing MnO ₆	n.r.	[31]
[Mn ₅ (poapH) ₆] ⁴⁺	5Mn ^{II}	Trigonal bipyramid	⁵ / ₂	[32]
[Mn ₅ (phaapH) ₆] ⁴⁺	5Mn ^{II}	Trigonal bipyramid	⁵ / ₂	[33]
[Mn ₅ (PzCAP) ₆] ⁴⁺	5Mn ^{II}	Trigonal bipyramid	⁵ / ₂	[34]
[Mn ₅ O(OPh) ₈ (py) ₆]	5Mn ^{II}	Trigonal bipyramid	n.r.	[35]
[Mn ₅ (¹ L) ₂ (O ₂ CMe) ₂ (ClO ₄) ₂] ²⁺	5Mn ^{II}	Bow-tie	n.r.	[36]
[KMn ₅ O ₂ (² L) ₄ (O ₂ CMe) ₄ (MeOH) ₂ (H ₂ O)]	5Mn ^{II}	Bow-tie	0	[37]
[Mn ₅ (³ L) ₆] ²⁻	5Mn ^{II}	Linear	n.r.	[38]
[Mn ₅ (C8AH ₄)(OH) ₂ (DMF) ₅ (MeO) _{1.5} (RCO ₂) _{1.5}]	5Mn ^{II}	Tetragonal pyramid	n.r.	[39]
[Mn ₅ O(bpp) ₆] ³⁺	4Mn ^{II} Mn ^{III}	Trigonal bipyramid	3	[44]
[Mn ₅ (cat) ₄ (O ₂ C ^t Bu) ₂ (py) ₈] ⁺	4Mn ^{II} Mn ^{III}	Bow-tie	n.r.	[45]
[Mn ₅ O(⁶ L) ₃ (NO ₃)(OMe) ₂ (MeOH)] ¹⁺	3Mn ^{II} 2Mn ^{III}	Trigonal bipyramid	n.r.	[46]
[Mn ₅ (tmpen) ₆ (CN) ₁₂]	3Mn ^{II} 2Mn ^{III}	Trigonal bipyramid	¹¹ / ₂	[49]
[Mn ₅ (fastren) ₂ (H ₂ O) ₄]	3Mn ^{II} 2Mn ^{III}	Linear	⁷ / ₂	[53]
[Mn ₅ (⁷ LH ₂) ₃ (⁷ LH ₅)(MeOH) ₃] ⁴⁺	2Mn ^{II} 3Mn ^{III}	Trigonal bipyramid	2	[48]
[Mn ₅ O(⁸ L) ₃ X ₅] (X = Br, Cl)	2Mn ^{II} 3Mn ^{III}	Trigonal bipyramid	2	[50]
[Mn ₅ O(⁹ L)(O ₂ CC ₆ H ₄ C ₆ H ₅) ₅ (THF)]	2Mn ^{II} 3Mn ^{III}	Trigonal bipyramid	n.r.	[51]
[Mn ₅ O(salox) ₃ (N ₃) ₆ Br ₂] ³⁻	2Mn ^{II} 3Mn ^{III}	Trigonal bipyramid	11	[52]
[Mn ₅ (OH) ₂ (TBC[4]) ₂ (hmp) ₂ (DMF) ₆]	2Mn ^{II} 3Mn ^{III}	Twisted bow-tie	11	[54]
[Mn ₅ (¹⁰ LH) ₂ (¹⁰ L) ₂ (O ₂ CMe) ₄]	Mn ^{II} 4Mn ^{III}	Bow-tie	2	[40]
[Na ₂ Mn ₅ O ₂ (O ₂ CMe) ₄ (¹¹ L) ₄ (DMF) ₄ (H ₂ O)]	Mn ^{II} 4Mn ^{III}	Twisted bow-tie	n.r.	[55]
[Mn ₅ (O ₂ C ^t Bu) ₂ (cat) ₄ (py) ₈] ⁺	Mn ^{II} 4Mn ^{III}	Twisted bow-tie	n.r.	[56]
[Mn ₅ (shi) ₄ (O ₂ CMe)(DMF) ₆]	Mn ^{II} 4Mn ^{III}	Tetragonal pyramid	n.r.	[57]
[Mn ₅ (¹² L) ₂ (py) ₈ (N ₃) ₂]	Mn ^{II} 4Mn ^{III}	Hemicyclic crown	n.r.	[58]
[Mn ₅ O(⁴ L) ₄ (O ₂ CPh) ₃ (MeOH)]	5Mn ^{III}	Extended rhombus	2	[40]
[Mn ₅ O ₂ (O ₂ CMe) ₄ (² L) ₄] ¹⁻	5Mn ^{III}	Twisted bow-tie	0	[41]
[Mn ₅ O ₂ (phpH) ₃ (php) ₃ (OMe)(MeOH) ₂ (O ₂ CR)]	5Mn ^{III}	Edge-fused triangles	n.r.	[42]
[Mn ₅ O ₃ (^t BuPO ₃) ₂ (O ₂ CMe) ₃ (H ₂ O)(phen) ₂]	5Mn ^{III}	Basket-like	2	[43]
[Mn ₅ O(mpkO) ₅ (MeOhmp)(mpko-hmp)(H ₂ O)] ³⁺	4Mn ^{II} Mn ^{IV}	Trigonal bipyramid	⁷ / ₂	[59]
[Mn ₅ O ₂ (Et-sao) ₆ (OMe)(val)] ¹⁺	3Mn ^{III} 2Mn ^{IV}	Edge-fused triangles	2	[60]
[Mn ₅ O ₄ (phth) ₃ (phthH)(bpy) ₄] ⁺	Mn ^{II} 2Mn ^{III} 2Mn ^{IV}	Twisted bow-tie	⁷ / ₂	t.w.

^a Abbreviations: trazH = triazole; poapH = alkoxo, diazine ligand; phaapH = ditopic, diazine ligand; PzCAP = 5-methyl-N-[(1E)-1-(pyridin-2-yl)ethylidene]-1H-pyrazole-3-carbohydrazonic acid; py = pyridine; C8AH₈ = p-tert-butylcalix[8]arene; phpH₂ = 5(3)-(2-hydroxyphenyl)-3(5)-ethylpyrazole; phen = 1,10-phenanthroline; bppH = 3,5-bis(pyridin-2-yl)-pyrazole ligand; catH₂ = catechol; saloxH₂ = salicylaldoxime; tmpen = 3,4,7,8-tetramethyl-1,10-phenanthroline; fsatrenH₆ = 3-formylsalicylic acid; TBC[4] = p-tert-butylcalix[4]arene; hmpH = 2-hydroxymethylpyridine; shiH₃ = salicylhydroxamic acid; mpkoH = methyl(pyridin-2-yl)ketone oxime; MeOhmpH = methoxy(pyridine-2-yl)methanol; mpkohmp = (E)-1-(pyridin-2-yl) ethan-1-one O-(hydroxy(pyridin-2-yl)methyl) oxime; Et-saoH = (2-hydroxypropionophenoneoxime); val = valine. ¹LH₂ = [2 + 2] macrocycle; ²LH₂ = 1,2,4-triazole-based Schiff base ligand; ³LH₄ = N-(5-(2-hydroxyphenyl)-1,3,4-oxadiazol-2-yl)benzamide; ⁴LH₂ = 3,5-dibromosalicylidene-2-ethenamine; ⁵LH₂ = N-(2-hydroxy-3-methoxybenzyl)-3,5-diamino-1,2,4-triazole; ⁶LH₂ = 2,6-bis[5-(2-pyridinyl)-1H-pyrazole-3-yl]-pyridine; ⁷LH₅ = 2,2-bis(hydroxymethyl)-2,2'-nitritoltriethanol; ⁸LH₂ = Schiff-based ligand; ⁹LH₃ = derived from a pseudo-C₃ symmetric ligand; ¹⁰LH₂ = 3-(2-hydroxy-3,5-dibromobenzylideneamino)propane-1,2-diol; ¹¹LH₂ = 2-hydroxyphenyl-1,3,4-oxadiazole-2(3H)-thione; ¹²LH₆ = N,N'-bis(2-salicylhydrazide)isophthalohydrazide

^b Counterions and solvent molecules are omitted, n.r. = not reported, t.w. = this work

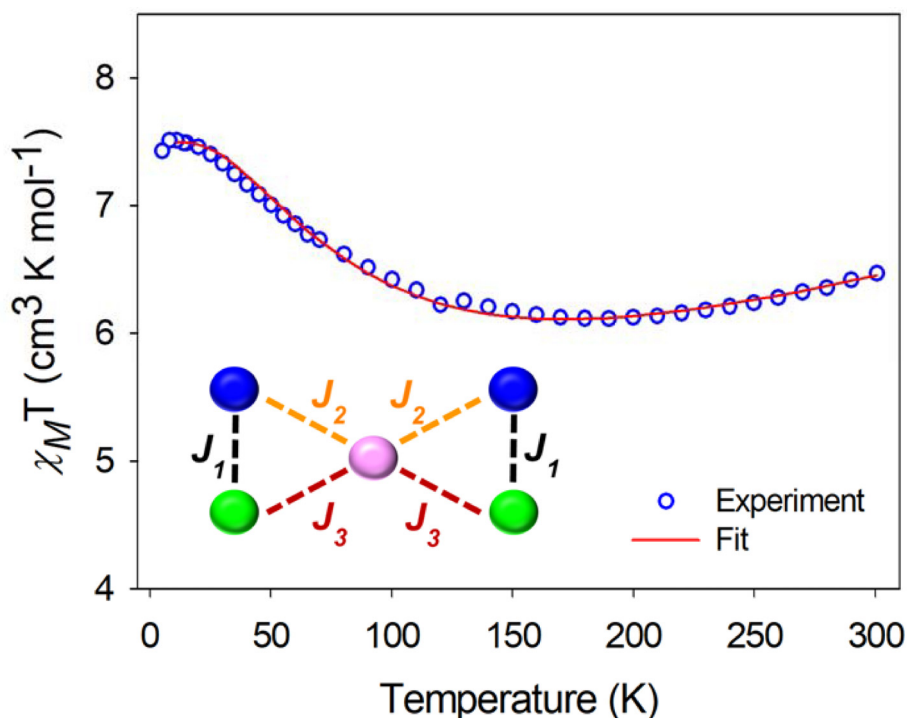


Fig. 3. χ_m vs. T data for complex **1**· $\frac{3}{2}$ H₂O. The solid red line is the fit using program PHI to the 3- J exchange-coupling model in the inset (Mn^{IV} blue; Mn^{III} green; Mn^{II} violet); see the text for the fit parameters. ((Color online.))

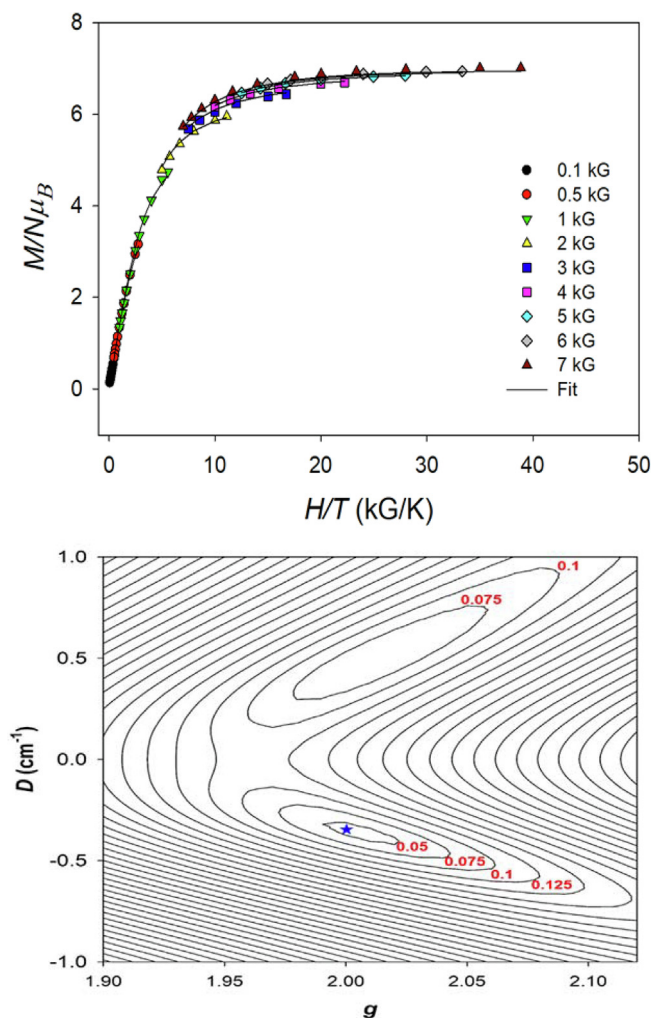


Fig. 4. (top) plot of reduced magnetization ($M/N\mu_B$) vs. H/T data for $1\cdot^{3/2}\text{H}_2\text{O}$ at the indicated applied dc fields. The solid lines are the fit of the data; see the text for the fit parameters. (bottom) root-mean-square g vs D error surface as a 2-D contour plot for the fit of $M/N\mu_B$ vs H/T for $1\cdot^{3/2}\text{H}_2\text{O}$. The asterisk indicates the best-fit minimum corresponding to the fit parameters in the text. ((Color online.))

$\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]^{n-}$, of the Mn_{12} SMMs [29]. In addition, to our knowledge this is the highest oxidation state Mn phthalate complex prepared to date, most of the others being Mn^{II} complexes and a few being Mn^{III} ones, including the giant $\text{K}_4[\text{Mn}_{18}\text{O}_{16}(\text{O}_2\text{CPh})_{22}(\text{phth})_2(-\text{H}_2\text{O})_4]$ [30].

There are many previously reported Mn_5 clusters with a wide variety of ligands (Table 4) [31–60], and only a few possess a bow-tie or twisted bow-tie structure similar to the cation of **1**; instead the most common metal topology is a trigonal bipyramid. Almost all known Mn_5 clusters of any topology contain Mn^{II} and/or Mn^{III} oxidation states and are thus at a lower oxidation state than **1**, primarily because they often contain few, if any, bridging $\mu_n\text{-O}^{2-}$ ions. Only two other clusters contain Mn^{IV} , and only the cation of **1** contains three oxidation states.

3.3. SQUID magnetometry

3.3.1. Dc susceptibility studies

Solid-state, variable-temperature dc magnetic susceptibility data in the 5.0–300 K range were collected on crushed microcrystalline samples of vacuum-dried $1\cdot^{3/2}\text{H}_2\text{O}$ restrained in eicosane to prevent torquing. $\chi_m T$ decreases with decreasing T from $6.47 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K to a minimum of $6.12 \text{ cm}^3 \text{ K mol}^{-1}$ at 180 K, and

then increases to a plateau maximum of $7.51 \text{ cm}^3 \text{ K mol}^{-1}$ at 8.0–10.0 K followed by a small decrease to $7.43 \text{ cm}^3 \text{ K mol}^{-1}$ at 5.0 K [Fig. 3]. The 300 K value is far below the spin-only ($g = 2.0$) value calculated for one Mn^{II} , two Mn^{III} , and three Mn^{IV} non-interacting ions ($14.13 \text{ cm}^3 \text{ K mol}^{-1}$), indicating the presence of strong antiferromagnetic (AF) exchange coupling, and the 8.0 K value indicates a ground state spin of $S = 7/2$ (spin-only value $7.88 \text{ cm}^3 \text{ K mol}^{-1}$). The small decrease below 8.0 K is assigned to zero-field splitting (ZFS) and/or weak AF intermolecular interactions.

Confirmation of the ground state of **1** came from magnetization (M) vs field (H) and T data collected in the 0.1–7.0 T and 1.8–10.0 K ranges, respectively. The data, plotted as reduced magnetization ($M/N\mu_B$) vs H/T in Fig. 4a, where N is Avogadro's number and μ_B is the Bohr magneton, were fit by diagonalization of the spin Hamiltonian matrix using the program MAGNET [22], which assumes that only the ground state is occupied, includes axial ZFS and the Zeeman interaction, and incorporates a full powder average. The corresponding spin Hamiltonian is given in Eq. (2), where $\hat{S}$ is the electron spin operator and $\hat{S}_z$ its projection onto the z -axis, D is the axial

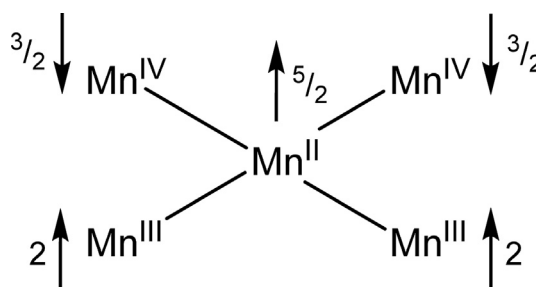
$$H = D\hat{S}_z^2 + g\mu_B\mu_0\hat{S}H \quad (2)$$

ZFS parameter, g is the electronic g factor, and μ_0 is the vacuum permeability. An excellent fit (solid lines in Fig. 4a) was obtained with $S = 7/2$, $g = 2.00(2)$, and $D = -0.36(3) \text{ cm}^{-1}$. The D vs g error surface (Fig. 4b) revealed a best-fit minimum rather soft in g giving the quoted uncertainties in the fit parameters. As is usually the case, a second fit with a positive D was also observed, but of poorer quality.

To obtain the exchange coupling constants (J_{ij}) in the Mn_5 cation, the dc $\chi_m T$ data in the 10.0–300 K range (to avoid the lower T decrease due to other effects) were fit to the 3- J model shown as an inset in Fig. 3. This assumes that the two $J(\text{Mn}^{\text{II}}\text{Mn}^{\text{IV}})$ interactions (J_1) are equivalent even though the cation has no virtual symmetry; nevertheless, it is a reasonable assumption based on the core structure. The same applies to the two $J(\text{Mn}^{\text{II}}\text{Mn}^{\text{IV}})$ (J_2) and two $J(\text{Mn}^{\text{II}}\text{Mn}^{\text{III}})$ (J_3) interactions. It also assumes next-nearest neighbor interactions are too weak to be significant in the data range employed. The corresponding spin Hamiltonian is given by Eq. (3).

$$H = -2J_1(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_4 \cdot \hat{S}_5) - 2J_2(\hat{S}_2 \cdot \hat{S}_3 + \hat{S}_3 \cdot \hat{S}_4) - 2J_3(\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_3 \cdot \hat{S}_5) \quad (3)$$

The resulting fit using PHI (solid line in Fig. 3) gave $J_1 = -116(3) \text{ cm}^{-1}$, $J_2 = -6.0(4) \text{ cm}^{-1}$, $J_3 = +3.8(8) \text{ cm}^{-1}$, and $g = 1.95$, with $\text{TIP} = 500 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ [61]. Strongly AF J_1 is in the typical range for $\{\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}\text{O}_2(\text{O}_2\text{CR})\}$ complexes [62], and weakly AF J_2 is in the typical range for $\text{Mn}^{\text{IV}}\text{-O}^{2-}\text{-Mn}^{\text{II}}$ couplings [59,63]. In addition, $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ couplings can be either weakly F or AF, so the value of J_3 is also reasonable [47,54,55,64,65]; different runs varying the



Scheme 1.

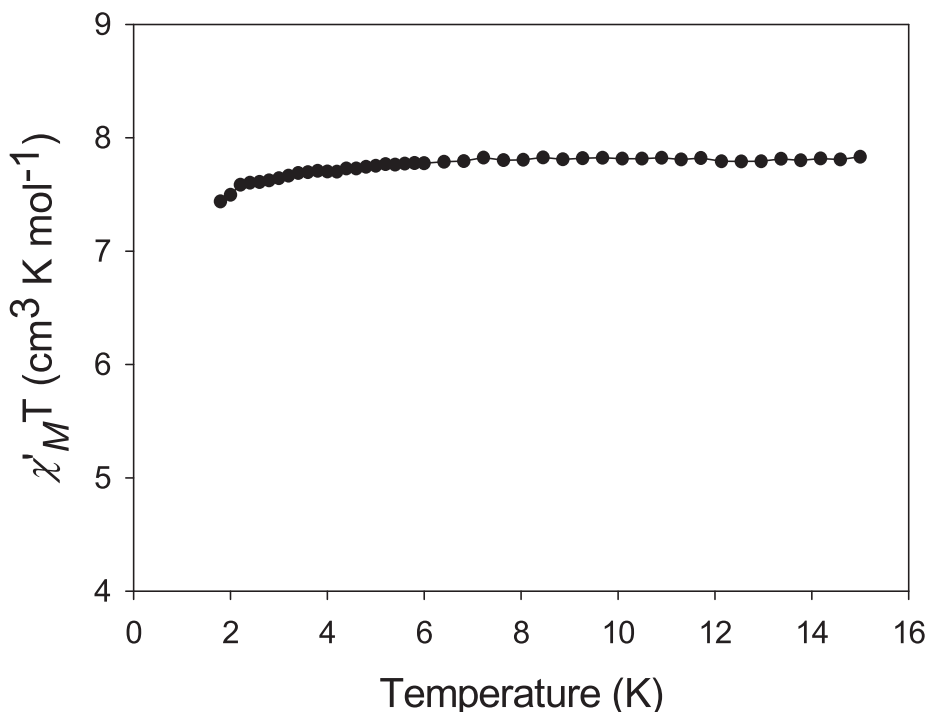


Fig. 5. In-phase (χ'_m , as $\chi'_m T$) vs T ac susceptibility for vacuum-dried $1 \cdot \frac{3}{2} \text{H}_2\text{O}$ at 1000 Hz. The solid line is a guide for the eye.

input value and sign for J_3 all gave a **F** output, so we are confident J_3 really is **F**. The obtained $J_1 - J_3$ thus give an $S = 7/2$ ground state, in agreement with the fit of the dc magnetization data above, arising from the spin vector alignments shown in Scheme 1. The first excited state is an $S = 5/2$ state at 68.4 cm^{-1} above the ground state. Note that there are no spin frustration effects (competing exchange interactions) operative.

3.3.2. Ac susceptibility studies

As an additional probe of the ground state, ac susceptibility data were collected for $1 \cdot \frac{3}{2} \text{H}_2\text{O}$ in the 1.8 – 15 K range at a 1000 Hz oscillation frequency. The in-phase ac susceptibility (χ'_m) plotted as $\chi'_m T$ vs T (Fig. 5) is essentially constant down to ~6 K and then decreases slightly. The plateau value above 6 K of $7.77 \text{ cm}^3 \text{ K mol}^{-1}$ is as expected for an $S = 7/2$ ground state with a g slightly less than 2.0, as expected for a $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ -containing system, and supports the conclusions from the dc studies. No signals were observed in the out-of-phase (χ''_m) ac susceptibility measurements down to 1.8 K, which is consistent with the low spin and low anisotropy, the latter due to the near-perpendicular Mn^{III} JT axes.

4. Conclusions

This is our first report of the use of the ‘reductive aggregation’ procedure with a dicarboxylic acid and a non-bridging chelate, and as might be expected it has led to a relatively low nuclearity Mn_5 cluster but one that nevertheless has multiple points of interest and novelty. It has a rare ‘twisted bow-tie’ Mn_5 topology and equally rare is the presence of three Mn oxidation states; as a result, it is the first Mn_5 bow-tie complex to contain Mn^{IV} ions. The latter is also the first Mn^{IV} phthalate complex. The magnetic properties are also interesting, with strong $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ AF exchange coupling dominating its behavior but the other couplings then facilitating a ground state spin of $S = 7/2$. This work thus emphasizes a greater utility of the reductive aggregation procedure to new cluster types than had been demonstrated for it previously. Further work is in progress.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

CCDC 2058971 contains the supplementary crystallographic data for $1 \cdot 11\text{MeOH}$. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.poly.2021.115141>.

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