Synthesis, structure and magnetism of the mixed-valent phosphonate cage, [Mn^{II}Mn$^{III}_{12}$(μ$_4$-O)$_6$(μ-OH)$_6$(O$_3$P–t-Bu)$_{10}$(OH$_2$)$_2$(DMF)$_4$]·[2MeOH·4DMF]

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ABSTRACT

The reaction of MnCl$_2$·4H$_2$O with t-BuPO$_3$H$_2$ in the presence of triethylamine afforded the tridecanuclear cage, [Mn^{II}Mn$^{III}_{12}$(μ$_4$-O)$_6$(μ-OH)$_6$(O$_3$P–t-Bu)$_{10}$(OH$_2$)$_2$(DMF)$_4$]·[2MeOH·4DMF] (**1**). The structural analysis of **1** reveals that it is a mixed-valent complex containing a [Mn^{II}Mn$^{III}_{12}$(μ$_4$-O)$_6$] core. The centre of the core is occupied by a Mn^{II} ion which is surrounded by 12 Mn^{III} ions. The latter are connected to each other by six μ-OH$^-$ and 10 t-BuPO$_3$$^{2-}$ ligands. The vacant coordination sites of six Mn^{III} ions situated in the periphery are occupied by four DMF and two water molecules. Magnetic studies on **1** reveal a frequency-dependent response which is characteristic of single-molecule magnets.

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1. Introduction

Interest in polynuclear manganese complexes in general and mixed-valent complexes in particular shot up considerably after the discovery that [Mn$^{IV}_4$Mn$^{III}_8$(μ$_3$-O)$_{12}$(O$_2$C–Me)$_{16}$(OH$_2$)$_4$]·2MeCO$_2$H·4H$_2$O (Mn$_{12}$-acetate) [1] was a single-molecule magnet (SMM) that showed magnetic behavior which is reminiscent of bulk magnetic behavior. This discovery simultaneously created enormous research activity in molecular magnetism as well as in polynuclear transition metal complexes. In Mn$_{12}$-acetate [1] itself two types of manganese sites are present: A central cube of Mn^{IV} sites surrounded by a peripheral ring of Mn^{III} sites. The overall magnetic spin ground state of Mn$_{12}$-acetate is S = 10. Detailed magnetic analysis of Mn$_{12}$-acetate and other polynuclear transition metal complexes revealed that the two most important criterions for a molecule to be an SMM are a large ground state spin and an overall magnetic anisotropy [2–4]. Subsequently, several polynuclear manganese complexes have been prepared [5–7], with the highest nuclearity being 84 [8]. All of these compounds have been prepared by the use of bi/polydentate ligands including carboxylates. In recent years the use of organophosphonate ligands for the preparation of polynuclear complexes is becoming prevalent. This multi-site coordinating ligand system, [RPO$_3$]$^{2-}$, can bind to as many as nine metal centers (Chart 1). We and others have shown the utility of this family of ligands for the assembly of a large number of interesting molecular transition metal [9–11] and main-group element [12–14] containing assemblies. In view of this it was of interest for us to examine if phosphonates can be used to prepare polynuclear manganese complexes. A perusal of the literature revealed that two mixed-valent and homo-valent molecular Mn$_{13}$ aggregates were known [15]. These were prepared by the use of C$_6$H$_{11}$PO$_3$$^{2-}$ and t-BuPO$_3$$^{2-}$ ligands. Since the structure of transition metal phosphonates is often dictated also by the nature of ancillary ligand [9–11] we experimented the synthesis *without* the use of an ancillary ligand. It might be pointed out that in this endeavor, recently we have reported carboxylate-free di-, tri- and tetranuclear Mn(II) phosphonate cages. [16]. The current work describes the mixed-valent molecular manganese phosphonate cage, [Mn^{II}Mn$^{III}_{12}$(μ$_4$-O)$_6$(μ-OH)$_6$(O$_3$P–t-Bu)$_{10}$(OH$_2$)$_2$ (DMF)$_4$]·[2MeOH·4DMF] (**1**). The vacant coordination site of six Mn^{III} ions on the periphery is occupied by four solvent DMF and two water molecules. The complex **1** was characterized by ESI-MS and Single Crystal X-ray analysis. Detailed magnetic studies have also been carried out on **1**. The molecular structure of **1** is similar to that of two previously known Mn$_{13}$ aggregates [15].
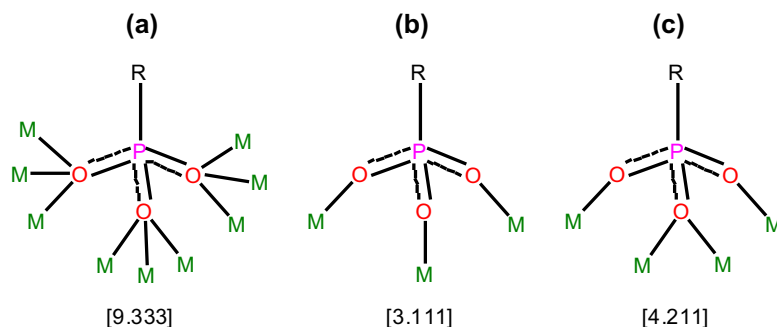

Chart 1. Metal coordination modes of phosphonate ligand given with Harris notation [20]. (a) Maximum possible coordination by a single ligand; (b) and (c) coordination modes observed with **1**.

Magnetic studies of **1** showed a frequency-dependent out-of-phase signal which is characteristic of a single-molecule magnet.

2. Experimental

2.1. Reagents and instrumentation

Solvents and other general reagents used in this work were purified according to standard procedures [17]. $MnCl_2·4H_2O$, $AlCl_3$, PCl_3, Et_3N and *tert*-butyl chloride (s.d. Fine Chemicals, India) were used as received. *tert*-Butylphosphonic acid (t-$BuPO_3H_2$) was prepared by following the literature procedure [18]. ^1H and ^{31}P NMR were recorded on a JEOL-JNM LAMBDA 400 model NMR spectrometer operating at 400.0 and 161.7 MHz respectively, in $CDCl_3$ solutions. Chemical shifts are referenced with respect to tetramethylsilane. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FT IR spectrophotometer operating between 400 and 4000 cm^{-1}. Elemental analysis of the vacuum-dried compound **1** was obtained using a Thermoquest CE instrument CHNS-O, EA/110 model. ESI-MS spectra were recorded on a MICROMASS QUAT-TRO II triple quadrupole mass spectrometer. Thermogravimetric analyses (heating rate of 10 °C/min) were carried out on a Perkin-Elmer Pyris 6 machine under argon atmosphere. Magnetic measurements were made using a Quantum Design MPMS-5XL SQUID magnetometer using the DC measurement mode. Polycrystalline samples were loaded into gelatin capsules mounted on a carbon-fibre rod. Susceptibility data were taken on cooling.

2.2. Synthesis of $[Mn^{II}Mn^{III}_{12}(\mu_4\text{-}O)_6(\mu\text{-}OH)_6(O_3P\text{–}t\text{-}Bu)_{10}(OH_2)_2(DMF)_4]·[2MeOH·4DMF]$

A mixture of $MnCl_2·4H_2O$ (0.278 g, 1.40 mmol) and t-$BuPO_3H_2$ (0.193 g, 1.40 mmol) in MeOH (35 mL) was stirred at room temperature for 30 min and Et_3N (0.282 g, 2.80 mmol) was added. The resulting brown turbid reaction mixture was stirred for additional 12 h and evaporated to dryness. The residue obtained was re-dissolved in DMF, filtered and kept for crystallization. Block-shaped dark brown crystals of **1** were collected after 10–15 days. Yield: 0.17 g (52% based on Mn; isolated crystals). *Anal.* Calc. for $C_{66}H_{164}N_8O_{54}P_{10}Mn_{13}$ (2957.96): C, 26.80; H, 5.59; N, 3.79. Found: C, 26.88; H, 5.62; N, 3.75%. IR (v/cm^{-1}): 3422(br), 2949(s), 2925(w), 2868(w), 1658(s), 1478(s), 1457(w), 1390(s), 1297(w), 1102(s), 1068(s), 1003(s, 834(s), 781(s), 669(s), 598(s), 554(s), 500(s). ESI-HRMS (m/z): 2273.4697, $[Mn_{13}(O)_6(OH)_6(O_3P\text{–}t\text{-}Bu)_{10} + H]^+$; 2373.5742, $[Mn_{13}(O)_6(OH)_6(O_3P\text{–}t\text{-}Bu)_{10} + EtOH + 3H_2O + H]^+$.

2.3. X-ray crystallography

A single-crystal X-ray structural study of **1** was performed on a Bruker SMART APEX CCD diffractometer equipped with an Oxford low-temperature cooling attachment. Data were collected using a graphite-monochromated Mo Kα radiation (λ_α = 0.71073 Å). Crystals did not degrade/decompose during the data collection. Data collection, structure solution and refinement were performed using SMART, SAINT and SHELXTL programs respectively [19a–f]. All the non-hydrogen atoms were refined anisotropically using full-matrix least-square procedures. All the hydrogen atoms were included in idealized positions and a riding model was used. All the lattice solvent molecules (two MeOH and four DMF) could not be modelled satisfactorily due to the presence of heavy disorder. Therefore PLATON/"SQUEEZE" [19g,19h] program was used to remove those disordered solvent molecules and obtained the total electron count of 762 per unit cell which corresponds to 190.5 electrons per molecule (Z = 4) and was assigned to two MeOH and four DMF molecules. The crystallographic parameters for **1** are given in the Table 1. All the mean plane analyses as well as molecular drawings were obtained from DIAMOND (version 3.1).

Table 1
Crystal data and structure refinement parameters of **1**.

Compound	**1**
Formula	$C_{52}H_{128}Mn_{13}N_4O_{48}P_{10}$
Formula weight	2601.50
T (K)	100(2)
Crystal system	monoclinic
Space group	$C2/c$
Unit cell dimensions	
a (Å)	28.966(7)
b (Å)	15.799(3)
c (Å)	28.110(7)
α (°)	90
β (°)	110.287(8)
γ (°)	90
V (Å^3)	12066(5)
Z	4
D_{calc} (Mg m^{-3})	1.432
Absorption coefficient (mm^{-1})	1.514
$F(000)$	5308
Crystal size (mm^3)	0.35 × 0.25 × 0.25
θ (°)	1.79–25.27
Limiting indices	$-34 \leqslant h \leqslant 32$, $0 \leqslant k \leqslant 18$, $0 \leqslant l \leqslant 33$
Reflections collected	34345
Unique reflections [R_{int}]	10950 [0.0991]
Completeness to θ	99.6% (25.27°)
Data/restraints/parameters	10950/5/550
Good-ness-of fit (GOF) on F^2	1.154
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.1160, wR_2 = 0.3115
R indices (all data)	R_1 = 0.1511, wR_2 = 0.3421
Largest residual peaks (e Å^{-3})	1.875 and −1.225

3. Results and discussion

3.1. Synthesis and structure

The 1:1 reaction between $MnCl_2 \cdot 4H_2O$ and t-$BuPO_3H_2$ in methanol, in the presence of two equivalents of triethylamine, at room temperature afforded **1** which could be recrystallized from DMF (see Section 2).

As will be described later, **1** is a mixed-valent compound possessing twelve Mn^{III} and one Mn^{II} centers. The conversion of Mn^{II} to Mn^{III} occurs as a result of aerial oxidation. The structural integrity of **1** was probed by ESI-MS, revealed the presence of peaks at m/z = 2273.4697 and 2373.5742 which are assigned to $[Mn_{13}(O)_6(OH)_6(O_3P-t-Bu)_{10} + H]^+$ and $[Mn_{13}(O)_6(OH)_6(O_3P-t-Bu)_{10} + EtOH + 3H_2O + H]^+$ ions respectively (Fig. 1). These observations indicate that the Mn_{13} core remains intact in solution.

The molecular structure of **1** (Fig. 2a and Scheme 1) was determined by single crystal X-ray crystallography which reveals that the crystal lattice contains both coordinated and uncoordinated solvent molecules (*vide infra*). Cage **1** crystallized in the monoclinic crystal system (space group: $C2/c$), one-half of the molecule is present in the asymmetric unit with an inversion center. The various coordination modes of the phosphonate ligands observed in **1** are summarized in Chart 1 [20]. The crystallographic parameters for **1** are given in Table 1 and selected bond parameters are summarized in Tables 2 and 3.

The cage **1** consists of 13 Mn centers, six O^{2-} and six $[OH]^-$ groups and 10 dianionic phosphonate ligands (Fig. 2a). In addition, the coordination needs of six peripheral manganese ions are fulfilled by two water and four DMF molecules. The oxidation state of each Mn site, oxo- and hydroxo-bridges in the cage was inferred from bond valence sum (BVS) analysis (Table 4) [10a,21]. Accordingly, of the 13 managanese centers, one is divalent (Mn7) which is present at the center of the cage while the rest are trivalent. The core of **1** consists of a central $[Mn^{II}Mn^{III}_6(\mu_4\text{-}O)_6]$ disc (Fig. 2b). The latter is connected with three Mn^{III} ions each on its top and bottom face respectively through μ_4-O and μ-OH ligands (Fig. 2b). The $[Mn^{II}Mn^{III}_6(\mu_4\text{-}O)_6]$ disc (Fig. 2b) is made up of an Mn^{II} atom (Mn7) at the center, surrounded by six other Mn^{III} atoms (Mn4, Mn5, Mn6, Mn4*, Mn5* and Mn6*) arranged in a hexagon, and are bridged by six μ_4-O atoms (O1, O2, O3, O1*, O2* and O3*). The hexagon of Mn^{III} atoms of the disc are further connected

Fig. 1. Isotopic distribution for $[Mn_{13}(O)_6(OH)_6(O_3P-t-Bu)_{10} + H]^+$ ion (m/z = 2273.4697) of **1** (a) and its simulated spectrum (b). Isotopic distribution for $[Mn_{13}(O)_6(OH)_6(O_3P-t-Bu)_{10} + EtOH + 3H_2O + H]^+$ ion (m/z = 2373.5742) of **1** (c) and its simulated spectrum (d).
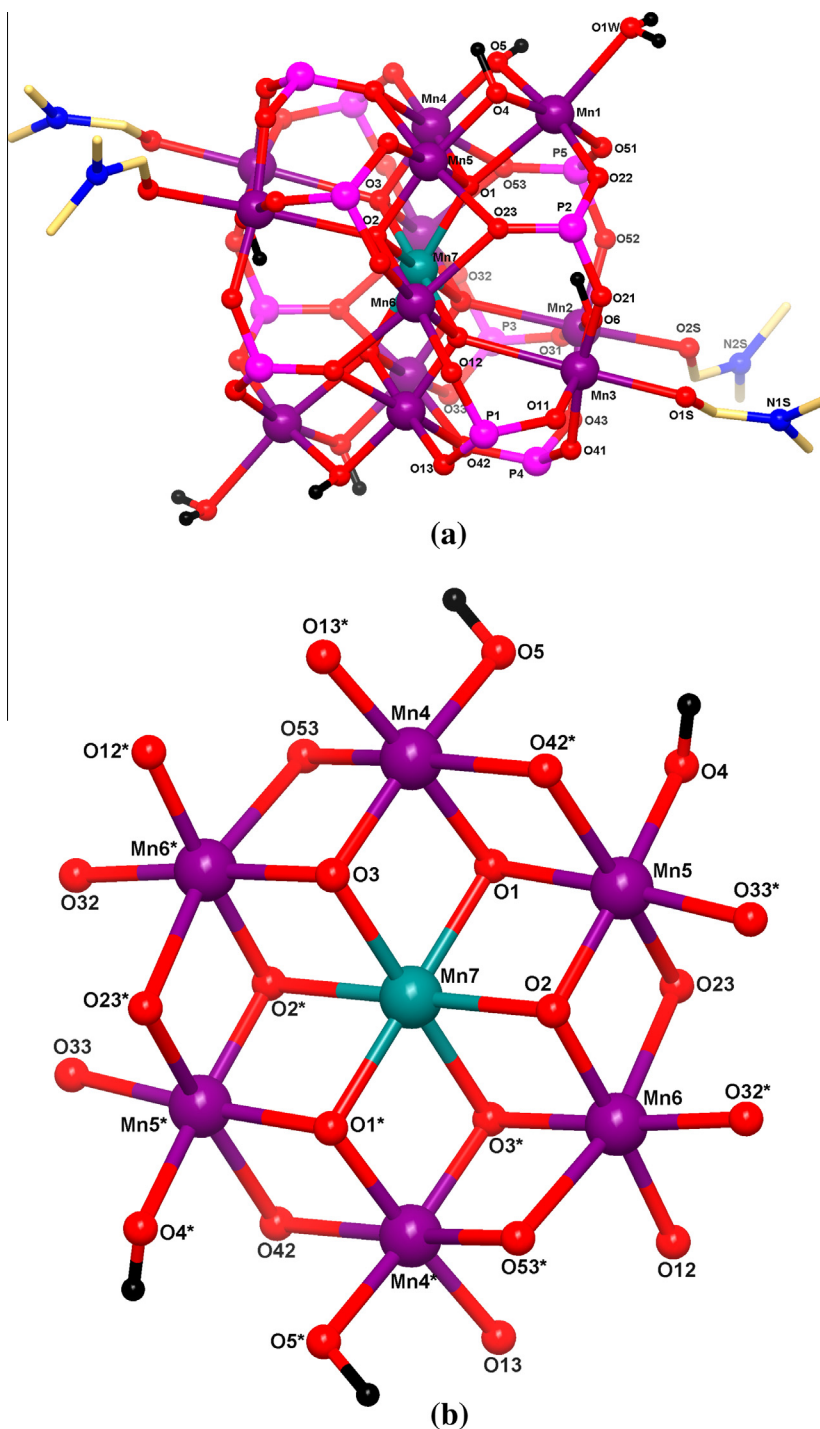
Fig. 2. (a) Molecular structure of **1**. All the *t*-butyl units on phosphonates and all the protons on carbon frameworks are removed; unlabelled atoms are symmetry related to labeled atoms. Color code for Mn sites: Mn^{II} = teal; Mn^{III} = violet; P = pink; O = red; N = blue. (b) View of the central [Mn^{II}Mn$^{III}_6(\mu_4$-O)$_6$] disc of cage **1**. Selected bond lengths (Å) and angles (°) are given in Tables 2 and 3. (Color online.)
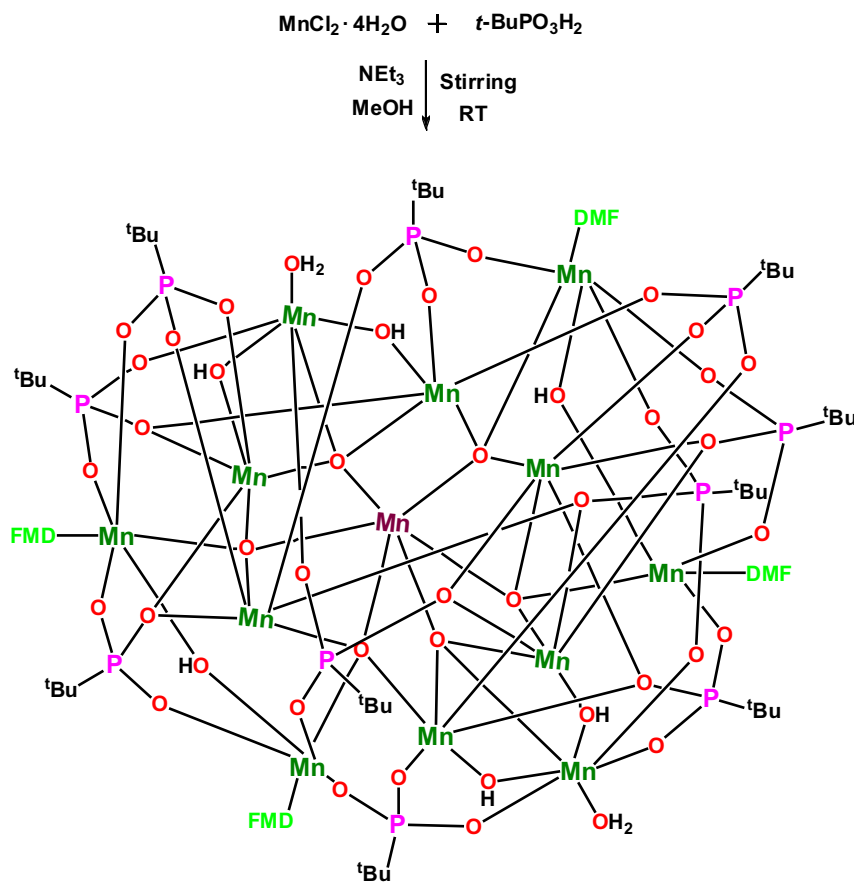
by six phosphonate oxygens (O23, O42, O53, O23*, O42* and O53*). The coordination geometry of all the manganese centres (6O) is distorted octahedral (see Supporting information).

To summarize, the core of cage **1** closely resembles two other literature precedents, [Mn^{II}Mn$^{III}_{12}(\mu_3$-O)$_6(\mu$-OH)$_6$(O$_3$P–C$_6$H$_{11}$)$_{10}$ (py)$_6$] (**2**) [15a] and [*n*-Bu$_4$N][Mn$^{III}_{13}(\mu_3$-O)$_6(\mu$-OH)$_2(\mu$-N$_3$)$_4$(O$_3$ P–*t*-Bu)$_{10}$(N$_3$)$_2$(HO$_2$C–Me)$_2$(OH$_2$)$_2$] (**3**) [15b] reported recently. However, there are some differences. For example, **3** is an anionic Mn$^{III}_{13}$ complex containing only Mn^{III} ions. It also contains azide and carboxylate ligands in the periphery (Table 5). On the other

hand **2** is a mixed-valent complex similar to **1**. However, the nature of phosphonate ligand is different (C$_6$H$_{11}$PO$_3^{2-}$); also the peripheral coordination sphere is different (Table 5).

3.2. Magnetic studies

Fig. 3 shows the variable-temperature dc magnetic susceptibilities of complex **1**. The χT data are measured in an applied field of 0.1 T and exhibit a significant increase on cooling from 150 to 3 K characteristic of the action of ferromagnetic interactions between

$$\text{MnCl}_2 \cdot 4\text{H}_2\text{O} \quad + \quad t\text{-BuPO}_3\text{H}_2$$

Scheme 1. Synthesis of **1**.

Table 2
Selected Mn–O bond lengths (Å) of complex **1**. See Fig. 2 for atom numbering scheme.

Mn(1)–O(51) 1.920(7)	Mn(3)–O(41) 1.895(7)	Mn(5)–O(23) 2.170(7)
Mn(1)–O(22) 1.923(7)	Mn(3)–O(6) 1.971(7)	Mn(5)–O(42)*2.217(7)
Mn(1)–O(4) 1.924(7)	Mn(3)–O(1S) 2.218(12)	Mn(6)–O(12) 1.916(7)
Mn(1)–O(5) 1.961(8)	Mn(3)–O3 2.570(7)	Mn(6)–O(32)*1.918(6)
Mn(1)–O(1) 2.307(7)	Mn(4)–O(3) 1.867(7)	Mn(6)–O(2) 1.941(6)
Mn(1)–O(1W) 2.3702(13)	Mn(4)–O(13)*1.924(7)	Mn(6)–O(3)*1.946(6)
Mn(2)–O(31) 1.843(8)	Mn(4)–O(1) 1.931(7)	Mn(6)–O(53)*2.248(7)
Mn(2)–O(43) 1.859(7)	Mn(4)–O(5) 1.952(8)	Mn(6)–O(23) 2.250(7)
Mn(2)–O(52) 1.879(8)	Mn(4)–O(53) 2.189(7)	Mn(7)–O(1)*1.999(7)
Mn(2)–O(6) 1.929(7)	Mn(4)–O(42)*2.214(7)	Mn(7)–O(1) 1.999(7)
Mn(2)–O(2S) 2.266(9)	Mn(5)–O(2) 1.870(7)	Mn(7)–O(3)*2.093(7)
Mn(2)–O(2)*2.509(7)	Mn(5)–O(33)*1.940(7)	Mn(7)–O(3) 2.093(7)
Mn(3)–O(21) 1.868(7)	Mn(5)–O(1) 1.957(7)	Mn(7)–O(2) 2.119(7)
Mn(3)–O(11) 1.869(7)	Mn(5)–O(4) 1.964(7)	Mn(7)–O(2)* 2.119(7)

Table 3
Selected Mn–O–Mn bond angles (°) of complex **1**. See Fig. 2 for atom numbering scheme.

Mn(4)–O(1)–Mn(5) 106.2(3)	Mn(5)–O(2)–Mn(7) 98.6(3)	Mn(6)*–O(3)–Mn(7) 97.5(3)
Mn(4)–O(1)–Mn(7) 101.0(3)	Mn(6)–O(2)–Mn(7) 96.9(3)	Mn(1)–O(4)–Mn(5) 102.5(3)
Mn(5)–O(1)–Mn(7) 99.9(3)	Mn(5)–O(2)–Mn(2)* 110.9(3)	Mn(4)–O(5)–Mn(1) 102.3(3)
Mn(4)–O(1)–Mn(1) 91.5(3)	Mn(6)–O(2)–Mn(2)* 119.1(3)	Mn(2)–O(6)–Mn(3) 140.4(4)
Mn(5)–O(1)–Mn(1) 90.2(3)	Mn(7)–O(2)–Mn(2)* 124.0(3)	Mn(4)–O(53)–Mn(6)* 84.7(2)
Mn(7)–O(1)–Mn(1) 160.9(3)	Mn(4)–O(3)–Mn(6)* 103.2(3)	Mn(5)–O(23)–Mn(6) 85.5(3)
Mn(5)–O(2)–Mn(6) 103.9(3)	Mn(4)–O(3)–Mn(7) 99.8(3)	Mn(4)*–O(42)–Mn(5) *89.2(2)

Table 4
Bond valence sum analysis (BVS) [10,21] for Mn sites in **1**.

Atom site	BVS			Assigned OS	Atom site	BVS	Assigned OS
	$\text{Mn}^{II}\text{–O}$	$\text{Mn}^{III}\text{–O}$	$\text{Mn}^{IV}\text{–O}$				
Mn1	2.976	2.722	2.859	Mn^{3+}	O1	1.996	O^{2-}
Mn2	3.355	3.067	3.223	Mn^{3+}	O2	1.892	O^{2-}
Mn3	3.197	2.924	3.073	Mn^{3+}	O3	1.897	O^{2-}
Mn4	3.266	2.988	3.140	Mn^{3+}	O4	1.234	OH^{-}
Mn5	3.185	2.913	3.061	Mn^{3+}	O5	1.191	OH^{-}
Mn6	3.101	2.837	2.981	Mn^{3+}	O6	1.214	OH^{-}
Mn7	2.654	2.248	2.552	Mn^{2+}			

the Mn centers dominating at these temperatures. Above 150 K the data decrease slowly on cooling. Taken together this behaviour is reminiscent of systems that display some kind of ferrimagnetic coupling. At 150 K the χT value reaches 4.2×10^{-4} m^3 K mol^{-1} (33.4 cm^3 K mol^{-1} in CGS). The value expected for a single Mn^{3+} ion ($S = 2$, $g = 2$) is 3.8×10^{-5} m^3 K mol^{-1} and for a single Mn^{2+} ion ($S = 5/2$, $g = 2$) is 5.5×10^{-5} m^3 K mol^{-1}. Thus for a molecule consisting of twelve $S = 2$ ions and an $S = 5/2$, the high-temperature, spin-only value of χT would be expected to approach 5.1×10^{-4} m^3 K mol^{-1} (40.6 cm^3 K mol^{-1} in CGS). The actual value is much lower than this and is agreement with that found in the related compound **2** [15a]. The inset to Fig. 3 shows the magnetization measured at a temperature of 2.0 K. Following a swift rise at low fields the magnetization slowly increases for the entire field range, reaching 18.6 μB per Mn$_{13}$ molecule at 7 T. The fully-saturated moment for an ensemble of twelve Mn^{3+} ions ($S = 2$, $g = 2$) and a single Mn^{2+} ion ($S = 5/2$, $g = 2$) is 53 μB.

Table 5
List of structurally related tridecanuclear manganese-phosphonate cages.

Formula	Nature of the cage	Mn oxidation state	Phosphonate	Bridging groups	Peripheral (solvent) coordination
$[Mn^{II}Mn^{III}_{12}(\mu_4\text{-}O)_6(\mu\text{-}OH)_6(O_3P\text{-}tBu)_{10}(OH_2)_2(DMF)_4]\cdot[2MeOH\cdot4DMF]$ (**1**)[a]	neutral	Mn^{II}; 12 Mn^{III}	10 $t\text{-}BuPO_3$	6 $\mu_4\text{-}O$; 6 $\mu\text{-}OH$	2 H_2O; 4 DMF
$[Mn^{II}Mn^{III}_{12}(\mu_3\text{-}O)_6(\mu\text{-}OH)_6(O_3PC_6H_{11})_{10}(py)_6]$ (**2**)[b]	neutral	Mn^{II}; 12 Mn^{III}	10 $C_6H_{11}PO_3$	6 $\mu_4\text{-}O$; 6 $\mu\text{-}OH$	6 pyridine
$[n\text{-}Bu_4N][Mn^{III}_{13}(\mu_3\text{-}O)_6(\mu\text{-}OH)_2(\mu\text{-}N_3)_4(O_3P\text{-}tBu)_{10}(N_3)_2(HO_2C\text{-}Me)_2(OH_2)_2]$ (**3**)[c]	anionic	13 Mn^{III}	10 $t\text{-}BuPO_3$	6 $\mu_4\text{-}O$; 2 $\mu\text{-}OH$; 4 N_3	2 H_2O; 2 N_3; 2 Me–CO_2H

[a] This work.
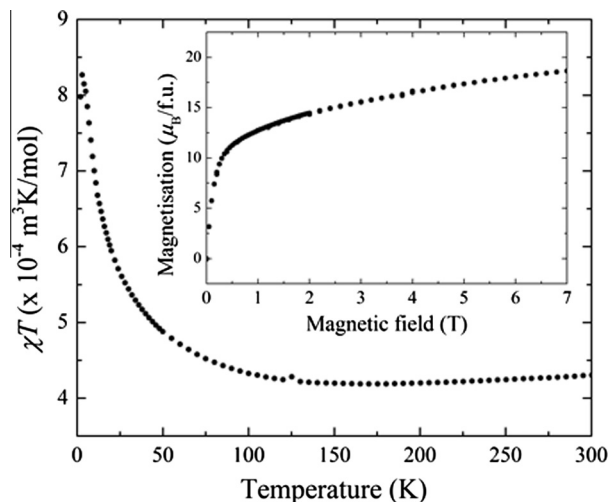[b] See Ref. [15a].
[c] See Ref. [15b].

Fig. 3. Temperature dependence of χT for complex **1** measured in an applied magnetic field of 0.1 T. The inset shows the magnetization measured at 2.0 K.
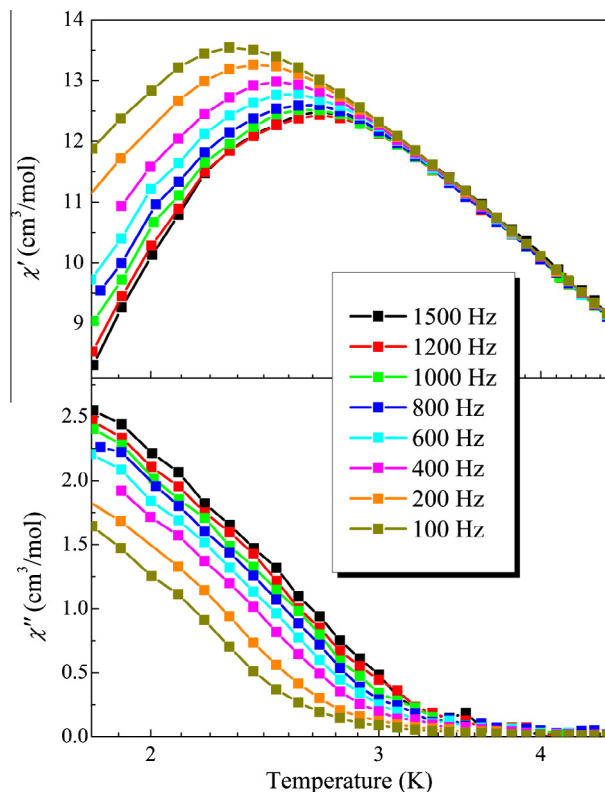

Fig. 4. Plot of (top) the in-phase (χ') and out-of-phase (χ'') ac susceptibility signal for complex **1** in a 4 Oe oscillating field at the indicated frequencies.

The dynamics of the magnetization has been investigated by measuring the frequency and temperature dependence of the ac magnetic susceptibility in zero static field. The in-phase (χ') and out-of-phase (χ'') ac susceptibility for complex **1** in an oscillating field of 0.1–1.5 kHz is shown in Fig. 4. Below 3.5 K, there is a frequency-dependent out-of-phase signal in the ac susceptibility, indicating SMM-like behaviour. Extrapolation of the 0.1 kHz $\chi'T$ above 3.5 K (Fig. S2) gives 4×10^{-4} m^3 K mol^{-1} (31.8 cm^3 K mol^{-1} in CGS) at 0 K, suggesting a molecular spin ground state of $S = 15/2$, which implies some level of antiferromagnetic interactions coexist with the ferromagnetic. Unfortunately, the peak maxima for the out-of-phase signals are not visible above 1.8 K at these frequencies; thus, the relaxation barrier could not be determined from the ac susceptibility measurements. Overall the DC magnetic properties of the cage **1** are distinct from that of other known Mn$_{13}$ phosphonate cages [15], while the AC response has some similarities, as illustrated in Table 6.

The plot of χ'' versus χ' (Fig. S3) reveals that the magnetization relaxation process for complex **1** is highly complicated and cannot be attributed to a single relaxation mechanism, since a simple semi-circle is not observed. The complicated magnetization relaxation process may arise from a number of factors including: spin–spin cross relaxation, dipolar interactions, low-lying excited states etc. Thus, no simple relaxation analysis can be applied to this system.

4. Conclusions

In summary, a mixed-valent manganese phosphonate cage, $[Mn^{II}Mn^{III}_{12}(\mu_4\text{-}O)_6(\mu\text{-}OH)_6(O_3P\text{-}tBu)_{10}(OH_2)_2(DMF)_4]\cdot[2MeOH\cdot4DMF]$ (**1**) was prepared by the reaction of MnCl$_2$·4H$_2$O with t-BuPO$_3$H$_2$ in the presence of triethylamine. In general, molecular phosphonates are accessed through the use of sterically hindered phosphonic acids and ancillary ligands. The assembly of **1** was accomplished without the use of ancillary ligands. Cage **1** is a mixed-valent complex containing a central Mn^{II} surrounded by twelve Mn^{III} ions. Detailed magnetic studies of **1** reveal a slow relaxation of magnetization which is indicative of a single-molecule magnet behaviour. We are currently investigating the modulation of the nuclearity of polynuclear Mn^{II}/Mn^{III} and Mn^{III} clusters by varying the type of phosphonate ligands.

Table 6
Comparison of Magnetic Features of Mn_{13} cages.

Compound	χT vs. T	χ'' vs. T	Ground-state spin	Magnetic property	Refs.
$[Mn^{II}Mn^{III}_{12}(\mu_4\text{-}O)_6(\mu\text{-}OH)_6(O_3PtBu)_{10}(OH_2)_2(DMF)_4]\cdot$ $[2MeOH\cdot 4DMF]$ (**1**)	dominant ferromagnetic interactions between Mn centers at low temperatures	frequency dependence response; no peak maximum is observed down to 1.8 K	7.5	SMM-like behaviour	this work
$[Mn^{II}Mn^{III}_{12}(\mu_3\text{-}O)_6(\mu\text{-}OH)_6(O_3PC_6H_{11})_{10}(py)_6]$ (**2**)	antiferromagnetic interactions between the Mn centers	frequency dependence response; no peak maximum is observed down to 1.7 K	3.5	Slow magnetic relaxation	[15a]
$[n\text{-}Bu_4N][Mn^{III}_{13}(\mu_3\text{-}O)_6(\mu\text{-}OH)_2(\mu\text{-}N_3)_4(O_3PtBu)_{10}$ $(N_3)_2(HO_2C\text{-}Me)_2(OH_2)_2]$ (**3**)	antiferromagnetic interactions between the Mn(III) atoms	frequency dependence response; no peak maximum is observed down to 2 K	4	SMM-like behaviour	[15b]

Appendix A. Supplementary data

CCDC 950232 contains the supplementary crystallographic data for compound **1**. 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 associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2014.01.017.

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