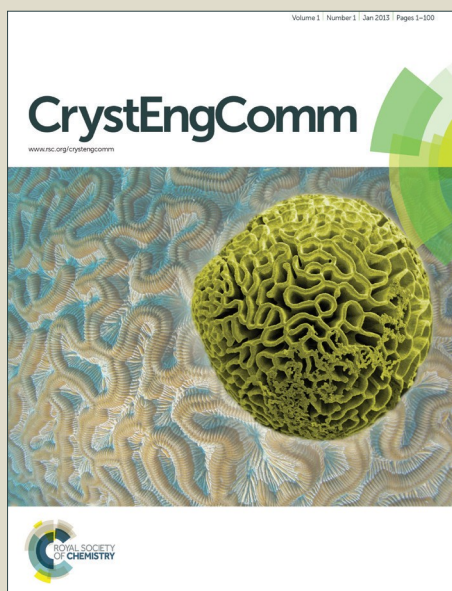


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Synthesis, crystal structures and magnetic properties of a family of manganese phosphonate clusters with diverse structures

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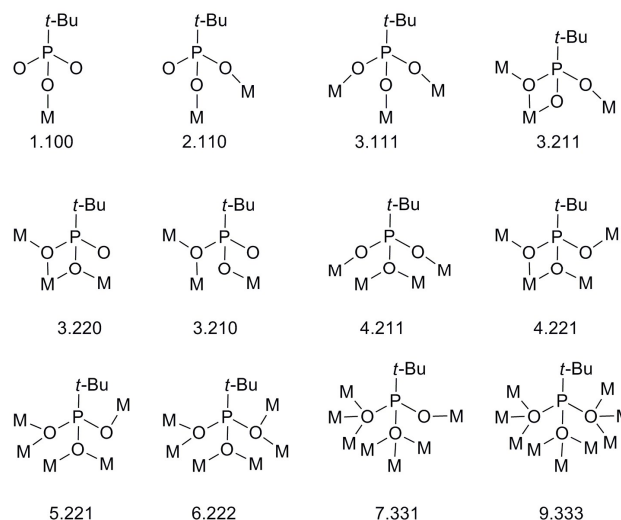
Jin-ying Liu^{a,b}, Cheng-bing Ma^a, Hui Chen^{a,b}, and Chang-neng Chen^{a*}

Four novel manganese phosphonate clusters: $\text{Cl} @ [\text{Mn}_6(\text{t-BuPO}_3)_8(\text{H}_2\text{O})_2(\text{CH}_3\text{OH})_4][\text{OH}]$ (**1**), $\text{Br} @ [\text{Mn}_6(\text{t-BuPO}_3)_8(\text{H}_2\text{O})_2(\text{CH}_3\text{OH})_4][\text{OH}] \cdot 4\text{H}_2\text{O}$ (**2**), $[\text{Mn}_{13}\text{O}_6(\text{t-BuPO}_3)_{10}(\text{OH})_6(\text{CH}_3\text{OH})_6][\text{Mn}_{13}\text{O}_6(\text{t-BuPO}_3)_{10}(\text{OCH}_3)_6(\text{t-BuPO}_3)_2(\text{H}_2\text{O})_4] \cdot 2\text{CH}_3\text{OH} \cdot 10\text{H}_2\text{O}$ (**3**), and $[\text{Mn}_{15}\text{K}_2\text{O}_8(\text{t-BuPO}_3)_{10}(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_5\text{COO})_4(\text{H}_2\text{O})_8] \cdot 6\text{H}_2\text{O}$ (**4**) have been successfully synthesized in the presence of tert-butylphosphonic acid, carboxylic acid, NBU_4MnO_4 and different manganese sources. They were characterized by elemental analyses, IR spectra, thermogravimetric (TG) analyses, and single-crystal X-ray diffraction. Single-crystal structural analyses reveal the structures of **1–4** are diverse. The structure of cluster **1** is analogue to cluster **2**, which displays a cage arrangement with one halide ion (Cl^- , Br^-) lying inside the centre of the cage. Cluster **3** is a carboxylate-free manganese phosphonate cluster, consisting of two similar Mn_{13} structural units. Moreover, there exist two potassium ions and fifteen manganese ions in the hetero-metallic cluster **4**. In addition, Solid-state DC magnetic susceptibility measurements indicate the existence of overall antiferromagnetic (AF) exchange interactions between the Mn ions in all clusters.

Introduction

Polynuclear 3d metal clusters have attracted continuous interests in decades not only for their aesthetically fascinating structures, but also their potential applications in magnetic materials^[1] and biological system^[2]. Parts of these clusters possess high-spin ground states and easy-axis-type magnetic anisotropy that result in a significant energy barrier to the magnetic reversal and functioning as single molecule magnets (SMMs)^[3]. SMMs are individual molecules that behave as magnets below a certain blocking temperature at the molecular scale. They own the capacity to store information via their magnetic states^[3c,4], so they have potential applications in both quantum computing and high-density magnetic information storage devices^[3b,4-5]. So far, the search for SMMs has based chiefly on the various transition metal clusters^[6], including vanadium^[7], manganese^[8], iron^[9], cobalt^[10] and nickel^[11] polynuclear clusters. With respect to other 3d transition metal clusters, manganese clusters are researched most widely because they often display abnormally high spin ground states (S) display abnormally high spin ground states (S) and a large

Scheme 1. Coordination modes for $\text{t-BuPO}_3\text{H}^-$ and t-BuPO_3^{2-} ligands



zero field splitting parameters (D) (derived from the presence of Jahn–Teller distorted Mn^{III} ions).

Manganese clusters have been investigated extensively, and a series of products with various shapes have been reported^[1b,1c,12], which is also our group longstanding research interest^[13]. However, the ligands which used to prepare these clusters are mainly involving carboxylates and alkoxides groups^[8k,13d,14]. In fact, phosphonates can play a positive role as an excellent alternative candidate. Their mono RPO_3H^- or

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Electronic Supplementary Information (ESI) available: X-ray crystallographic data file in CIF format for CCDC 949167 (1), 949168 (2), 949170(3), and 949171 (4). For ESI and crystallographic data in CIF or other electronic format supplementary information available See DOI: 10.1039/x0xx00000x

dianionic RPO_3^{2-} groups own three O donors that can bind to various types of metal ions even nine metal ions simultaneously and show various coordination modes (Scheme 1). What is more, transition-metal phosphonate clusters could play a vital role in potential applications, such as ion exchange, catalysis, proton conductivity as well as magnetism material.^[15] Among the phosphonate ligands, the *tert*-butyl phosphonic acid (*t*-BuPO₃H₂) has been employed most widely, a number of polynuclear metal phosphonate clusters, such as Cu_x (*x* = 3, 4, 5, 6, 10, 12, 16)^[16], Mn_y (*y* = 4, 5, 6, 13, 15, 20)^[13i,13k,13l,17], Co_z (*z* = 6, 12, 13, 14, 15)^[18], Fe_l (*l* = 4, 5, 6, 8, 10, 13)^[19] have been reported. It has been found that a slight modification of the phosphonate ligands, like addition of different ancillary ligands or basic reagent, would result in various structures of phosphonate clusters.^[13i,13j,13l,20]

In an effort to obtain Mn-based phosphonate clusters with diverse architectures, we have tried to develop new routes to synthesize clusters with different manganese sources and/or carboxylate ions under similar reaction conditions. In our present work, we have successfully gained a family of manganese clusters with various nuclearity and shapes: Cl@[Mn₆(*t*-BuPO₃)₈(H₂O)₂(CH₃OH)₄][OH]·4H₂O (**1**), Br@[Mn₆(*t*-BuPO₃)₈(H₂O)₂(CH₃OH)₄][OH]·4H₂O (**2**), [Mn₁₃O₆(*t*-BuPO₃)₁₀(OH)₆(CH₃OH)₆][Mn₁₃O₆(*t*-BuPO₃)₁₀(OCH₃)₆(*t*-BuPO₃H₂)₂(H₂O)₄]·2CH₃OH·10H₂O (**3**), and [Mn₁₅K₂O₈(*t*-BuPO₃)₁₀(CH₃O)₄(C₆H₅COO)₄(H₂O)₈]·6H₂O (**4**). The structure of cluster **1** is analogue to cluster **2**, which displays an unprecedented cage arrangement with one halide ion (Cl[−], Br[−]) lying inside the centre of the cage, such fascinating structure is unprecedented in manganese clusters. Cluster **3** is a high nuclearity complex containing two similar Mn₁₃ structure units, it should be noted that a closed related complex [Mn^{II}Mn^{III}₁₂O₆(OH)₆(O₃PC₆H₁₁)₁₀(py)₆] similar to the Mn₁₃ unit was reported by Li-Min Zheng in 2008.^[21] Additionally, cluster **4** is an unusual heterometallic phosphonate cluster^[13j,22]. Herein, we will describe the preparation, single-crystal X-ray structures, and magnetic properties towards these four clusters.

Experimental

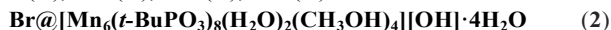
Materials and general methods

All manipulations were performed under aerobic conditions. NBu₄MnO₄ was prepared according to the literature.^[23] All the other reagents and solvents were of commercially available and used as received. The ligand *t*-BuPO₃H₂ was obtained from the company Alfa Aesar and its minimum purity is 99%. Elemental analyses (C, H and N) were performed on a Vario EL III CHNOS element analyser and infrared spectra (400–4000 cm^{−1}) were measured on a Nicolet Magna 750 FT-IR spectrophotometer using KBr pellets. Thermogravimetric analyses (TGA) were performed on a Mettler TGA/SDTA 851e analyzer with a heating rate of 10 °C min^{−1} from 30 to 800 °C under air atmosphere. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Mini Flex II diffractometer using CuKα radiation (λ = 1.54056 Å) under ambient conditions.

Synthesis of complexes 1–4

Cl@[Mn₆(*t*-BuPO₃)₈(H₂O)₂(CH₃OH)₄][OH] (**1**) Solid NBu₄MnO₄ (0.091 g, 0.25 mmol) in small portions was added to a

stirred solution of MnCl₂·4H₂O (0.20 g, 1 mmol) and EtCOOH (3.5 mL, 0.061 mol) in a mixture of MeCN (10 mL) and MeOH (10 mL), the brown mixture solution was added *tert*-butyl phosphonic acid (*t*-BuPO₃H₂) (0.070 g, 0.5 mmol) to yield a dark-brown solution which was stirred for 10 h at room temperature, then filtered. The filtrate was left to stand at room temperature for about two weeks, during which time black crystals were produced in 63% yield based on Mn. Elemental analysis (%) calcd for C₃₆H₉₃Mn₆O₃₁P₈Cl: C, 26.45; H, 5.68. Found: C, 26.47; H, 5.62. Selected IR data (KBr, cm^{−1}): 3423 (mb), 2974 (s), 1683 (w), 1599 (s), 1479 (m), 1413 (m), 1364 (m), 1293 (w), 1144 (vs), 1025 (vs), 910 (w), 833 (w), 716 (w), 654 (w), 576 (w), 492 (w), 466 (w).



This cluster was obtained by the same procedure to **1**, but MnCl₂·4H₂O and EtCOOH were replaced by MnBr₂·4H₂O and pivalic acid (pivH). Black crystals were produced in 17% yield based on Mn. Elemental analysis (%) calcd for C₃₆H₁₀₁Mn₆O₃₅P₈Br: C, 24.69; H, 5.77. Found: C, 24.47; H, 5.41. Selected IR data (KBr, cm^{−1}): 3420 (mb), 2984 (s), 1689 (w), 1590 (s), 1459 (m), 1413 (m), 1364 (m), 1293 (w), 1146 (vs), 1029 (vs), 915 (w), 836 (w), 711 (w), 654 (w), 495 (w), 469 (w).

[Mn₁₃O₆(*t*-BuPO₃)₁₀(OH)₆(CH₃OH)₆][Mn₁₃O₆(*t*-BuPO₃)₁₀(OCH₃)₆(*t*-BuPO₃H₂)₂(H₂O)₄]·2CH₃OH·10H₂O (**3**) This cluster was obtained by the same procedure to **1**, except that Mn(ClO₄)₂·6H₂O (0.36 g, 1 mmol) was instead of MnCl₂·4H₂O. The black crystals were produced in 53% yield based on Mn. Elemental analysis (%) calcd for C₁₀₂H₂₄₂Mn₂₆O₁₁₄P₂₂: C, 23.33; H, 5.17. Found: C, 23.72; H, 5.07. Selected IR data (KBr, cm^{−1}): 3418 (wb), 2974 (w), 2928 (w), 2871 (w), 1479 (s), 1459 (m), 1394 (w), 1364 (w), 1115 (s), 1056 (s), 1020 (s), 833 (w), 669 (w), 559 (m), 501 (w).

[Mn₁₅K₂O₈(*t*-BuPO₃)₁₀(CH₃O)₄(C₆H₅COO)₄(H₂O)₈]·6H₂O (**4**) This cluster was obtained by the same procedure to **1**, except that Mn(O₂CMe)₂·4H₂O, KI, as well as PhCOOH were instead of MnCl₂·4H₂O and EtCOOH. The brown crystals were produced in 51% yield based on Mn. Elemental analysis (%) calcd for C₇₂H₁₅₀K₂Mn₁₅O₆₄P₁₀: C, 26.58; H, 4.61. Found: C, 26.40; H, 4.60. Selected IR data (KBr, cm^{−1}): 3214 (mb), 2962 (s), 2903 (m), 2869 (m), 1574 (s), 1556 (vs), 1485 (vs), 1460 (s), 1418 (vs), 1361 (s), 1226 (s), 1123 (s), 1089 (s), 1042 (s), 903 (m), 873 (w), 789 (m), 749 (w), 634 (m), 614 (m), 603 (m), 561 (w), 537 (m), 497 (m), 476 (w), 418 (w).

Single-Crystal X-ray Structure Determination

The X-ray single-crystal data of clusters **1–4** were collected at 293 K on a Rigaku MERCURY CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å). The correction for absorption was performed using the program CrystalClear^[24]. The structures of clusters **1–4** were solved by direct methods and refined by full matrix least-squares techniques based on F² with all observed reflections performed with the SHELXTL-97 program package.^[25] The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were determined by geometrical calculations. The Squeeze^[26] instruction in the Platon^[27] software was applied to treat the data of the cluster **1**.

Scheme 2. Synthesis of clusters 1–4

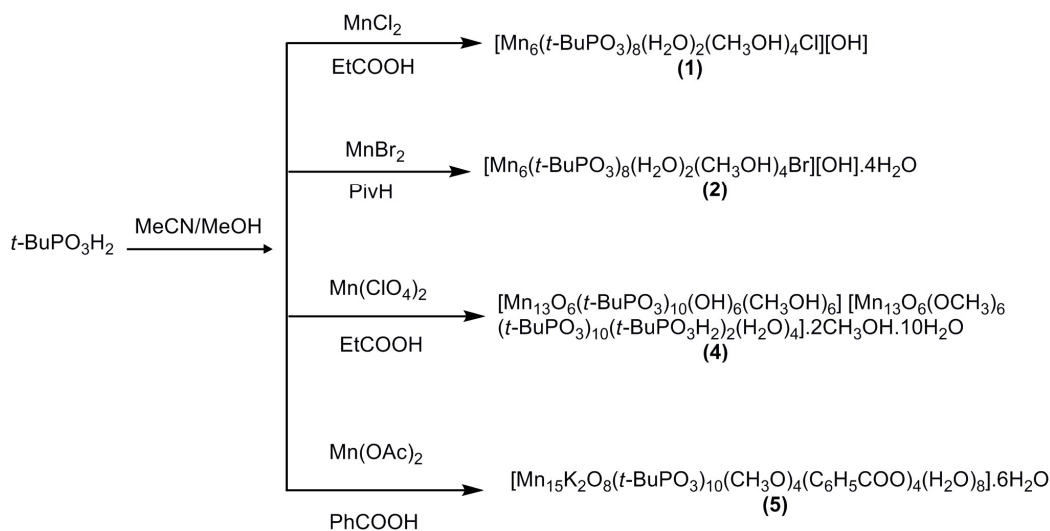


Table 1 Crystallographic data for clusters 1–4

Clusters	1	2	3	4
Chemical formula	$\text{C}_{36}\text{H}_{93}\text{Mn}_6\text{O}_{31}\text{P}_8\text{Cl}$	$\text{C}_{36}\text{H}_{101}\text{Mn}_6\text{O}_{35}\text{P}_8\text{Br}$	$\text{C}_{106}\text{H}_{282}\text{Mn}_{26}\text{O}_{112}\text{P}_{22}$	$\text{C}_{72}\text{H}_{128}\text{K}_2\text{Mn}_{15}\text{O}_{62}\text{P}_{10}$
$a / \text{\AA}$	14.2377(4)	14.2649(4)	15.30670(10)	17.496(8)
$b / \text{\AA}$	14.2377(4)	14.2649(4)	16.8196(5)	20.314(9)
$c / \text{\AA}$	21.5385(12)	21.6192(13)	24.5506(9)	18.017(8)
$\alpha / ^\circ$	90.00	90.00	87.508(7)	90.00
$\beta / ^\circ$	90.00	90.00	80.791(6)	96.771(7)
$\gamma / ^\circ$	90.00	90.00	70.565(5)	90.00
$V / \text{\AA}^3$	4366.1(3)	4399.2(3)	5883.3(3)	6259.5(5)
Z	2	2	1	2
Formula weight g mol^{-1}	1634.98	1751.34	5402.74	3253.70
Space group	$I4/m$	$I4/m$	P-1	$P2(1)/n$
Crystal system	Tetragonal	Tetragonal	Triclinic	Monoclinic
T / K	293	293	293	293
$\lambda / \text{\AA}$	0.7013	0.7013	0.7013	0.7013
Density (cal.) $/ \text{Mg m}^{-3}$	1.225	1.309	1.474	1.670
μ / mm^{-1}	1.077	1.500	1.568	1.712
R_1 [a] $[I > 2\sigma(I)]$	0.0589	0.0639	0.0587	0.0776
wR_2 [b] (all data)	0.2171	0.2164	0.173	0.2436
Goodness-of-fit	1.071	1.066	1.063	1.015

^a $R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|$. ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$.

Selected crystallographic data and refinement details for clusters 1–4 are displayed in Table 1.

Results and discussion

Synthetic procedures

Ability of phosphonic acid ligands to support various structure is well demonstrated by the growing number of reports on phosphonate metal clusters.²⁸ In the previous investigation on phosphonates, controlling different basic reagents, phosphonate ligands, or phosphoric acid, and ancillary ligands, researchers have obtained a large number of new structures.²⁸ During our study, we have explored the reaction system of tert-butyl phosphonic acid with different manganese sources $\text{MnR}_2\cdot 4\text{H}_2\text{O}$ ($R = \text{Cl}, \text{Br}, \text{ClO}_4, \text{CH}_3\text{COO}$) and/or carboxylate ions (EtCOOH , pivH , PhCOOH) in similar one-pot procedure, and successfully obtained four clusters with diverse structures and

high nuclearity, which is a valuable discovery for metal phosphonate chemistry. Previous works have proved that NBu_4MnO_4 in nonaqueous solvents represents a useful route to form higher oxidation state manganese clusters.^[28] The four clusters 1–4 are all prepared from the comproportionation reaction between Mn^{2+} and Mn^{7+} , which result in the Mn oxidation state of +3 in clusters 1 and 2, and mixed valence +2/+3 in clusters 3 and 4.

Reaction of $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ with NBu_4MnO_4 and $t\text{-BuPO}_3\text{H}_2$ in the presence of EtCOOH in a mixed solvent MeCN and MeOH resulted in the formation of cluster 1. Substituting $\text{MnBr}_2\cdot 4\text{H}_2\text{O}$ – pivH for $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ – EtCOOH leads to 2 with an analogous structure to 1 except for one bromide ion in the centre of the cage. However, using $\text{Mn}(\text{ClO}_4)_2\cdot 4\text{H}_2\text{O}$ in place of $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ in the same reaction system as 1 brings about a completely different kind of cluster 3. While using $\text{Mn}(\text{OAc})_2$ –

PhCOOH instead of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O} - \text{EtCOOH}$ and accompanying addition of KI in the same manner as **1**, we acquire a heptadeca-nuclear heterometallic cluster **4**. In fact, the reaction

Table 2. Selected bond lengths (Å) and angles (°) for cluster **1**

Mn(1)–O(2)#2	1.849(3)	Mn(2)–O(5)#4	1.847(3)
Mn(1)–O(2)	1.849(3)	Mn(2)–O(5)	1.847(3)
Mn(1)–O(2)#1	1.849(3)	Mn(2)–O(1)	1.865(3)
Mn(1)–O(2)#3	1.849(3)	Mn(2)–O(1)#4	1.865(3)
Mn(1)–O(3)	2.211(6)	Mn(2)–O(4)	2.192(4)
O(2)#2–Mn(1)–O(2)	178.0(2)	O(5)#4–Mn(2)–O(5)	90.2(3)
O(2)#2–Mn(1)–O(2) #1	89.983(4)	O(5)#4–Mn(2)–O(1)	177.36(15)
O(2)–Mn(1)–O(2)#1	89.983(4)	O(5)–Mn(2)–O(1)	90.1(2)
O(2)#2–Mn(1)–O(2) #3	89.983(4)	O(5)#4–Mn(2)–O(1) #4	90.1(2)
O(2)–Mn(1)–O(2)#3	89.983(4)	O(5)–Mn(2)–O(1)#4	177.36(15)
O(2)#2–Mn(1)–O(2) #3	178.0(2)	O(1)–Mn(2)–O(1)#4	89.5(3)
O(2)#2–Mn(1)–O(3)	90.98(10)	O(5)#4–Mn(2)–O(4)	90.48(13)
O(2)–Mn(1)–O(3)	90.98(10)	O(5)–Mn(2)–O(4)	90.48(13)
O(2)#1–Mn(1)–O(3)	90.98(10)	O(1)–Mn(2)–O(4)	92.14(13)
O(2)#3–Mn(1)–O(3)	90.98(10)	O(1)#4–Mn(2)–O(4)	92.14(13)

Symmetry transformations used to generate equivalent atoms: #1 -y+1, x+1, -z
#2 x, y, -z #3 y-1, -x+1, z #4 -y+1, x+1, z #5 -x, -y+2, z #6 y-1, -x+1, -z

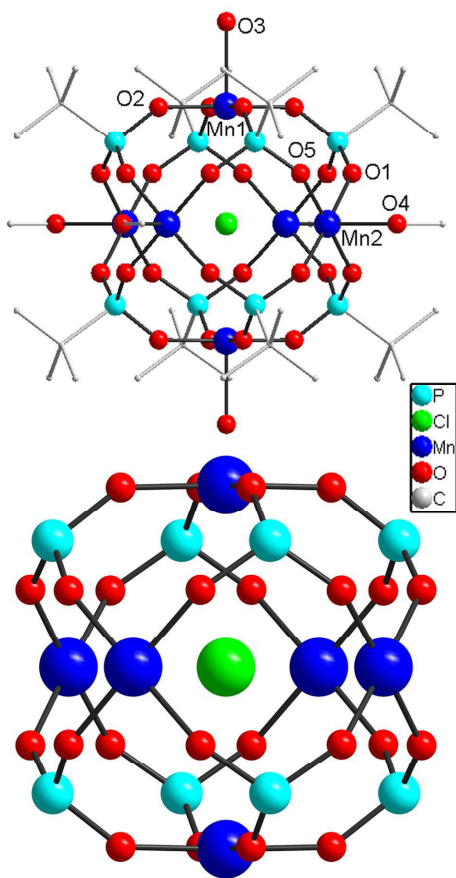


Figure 1. Molecular structure of cluster **1** (top); the core of cluster **1** (bottom). The noncoordinated solvent molecules and hydrogen atoms are omitted for clarity.

process of manganese complex is very complicated due to involve acid and redox chemistry, as well as structural arrangement. During preparation of clusters **1–4**, manganese sources play a key role in reaction for different anions, in addition, other synthetic factors has also some influence on the final products together with manganese sources, for example, using EtCOOH as acid medium to prepare clusters **2** and **4**, we would not obtain any crystal but sediment that we were unable to further characterize. It may be because the acidity of propionic acid is too strong for the system, and it is more suitable to use weak acid such as pivalic acid or benzoic acid as an alternative. A variety of reaction ratios, solvents and other conditions were also investigated. The mixture solvent MeCN–MeOH is the best choice for this reaction. When using individual MeCN, MeOH, or the other mixed solvents, we are unable to isolate any pure crystals for satisfactory characterization. The molar ratio of reagents also has influence on the reaction result, the ratio of tert-butylphosphonic acid and Mn^{2+} salts range from 1:1 to 2:1 is suitable, a 3:1 or higher proportion would lead to precipitate, while lower ratio would produce the same products with low yield. The synthetic route is shown in Scheme 2.

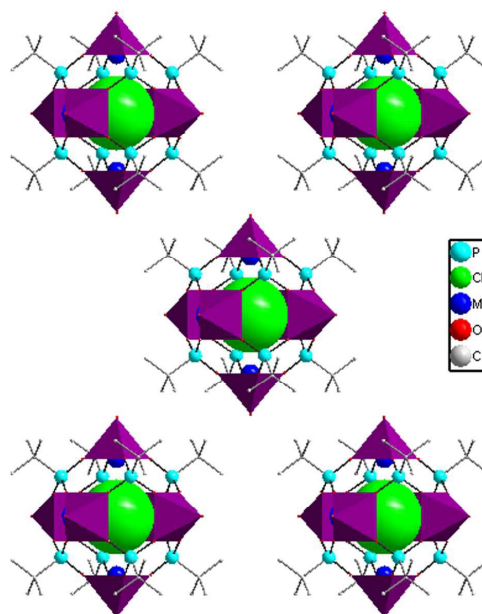


Figure 2. Polyhedral view along the b-axis of packing of cluster **1**. Hydrogen atoms are omitted for clarity.

Structure Description

Clusters **1** and **2** are similar in the structure only different in the central ion, the former is one chloridion and the latter is bromide ion, so the structure of cluster **1** will be described here as a representative (Figure 1), selected distances and angles are listed in Table 2, selected distances and angles of cluster **2** are listed in Table S1, supporting information. Cluster **1** crystallizes in the tetragonal space group $I4/m$, and the core $[\text{Mn}_6(\text{PO}_3)_8]^{2+}$ is a cage with one free Cl^- in the center of the cavity. The metal oxidation states and the level of protonation O atoms in the

molecule are established by the charge consideration, bond-valence-sum(BVS)^[23,29] calculations, as seen in Table 3, it indicates that six manganese atoms are all in +3 oxidation state and they are held together by six $\eta^1:\eta^1:\mu_3$ $t\text{-BuPO}_3^{2-}$ ligands. Peripheral ligation is completed by two H_2O groups on Mn1 and four protonated CH_3OH molecules on Mn2. All Mn ions are five-coordination in tetragonal pyramid geometry (Figure 2) by four oxygen atoms of $t\text{-BuPO}_3^{2-}$ ligands and a oxygen atom of H_2O or CH_3OH ligand, the bond length Mn1–O3 (2.211(6) Å) and Mn2–O4 (2.192(4) Å) is longer than the other bond lengths (1.85 ~ 1.87 Å), the distance between any two neighboring Mn ions is 4.40 Å and no significant intermolecular interactions can be observed in this cluster.

Table 3. Bond-valence sums for the Mn and O^a atoms of cluster 1

Atom	BVS	Assigned oxidation state	Group
Mn1	3.49	+3	
Mn2	3.38	+3	
O1	2.16		$t\text{-BuPO}_3^{2-}$
O2	2.16		$t\text{-BuPO}_3^{2-}$
O3	0.29		H_2O
O4	1.23		CH_3OH
O5	2.20		$t\text{-BuPO}_3^{2-}$

^a BVS values for O atoms of RO[−], ROH and H_2O groups are typically 1.8–2.0, 1.0–1.2 and 0–0.2, respectively, but can be affected by hydrogen bonding.

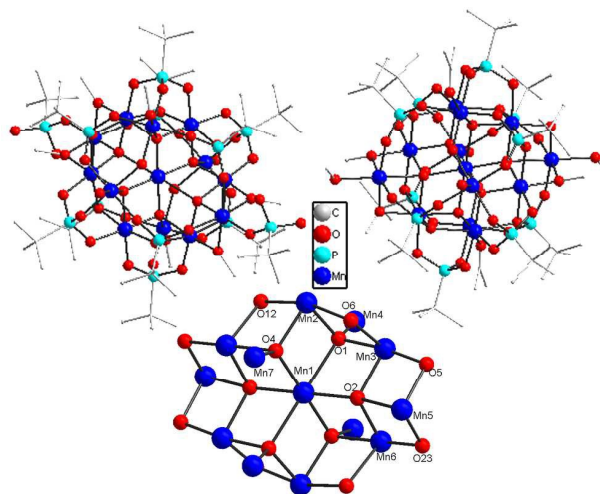


Figure 3 Molecular structure of cluster 3 (top); the core of cluster 3 (bottom). The noncoordinated solvent molecules and hydrogen atoms are omitted for clarity.

Several hexanuclear manganese clusters have been reported before^[8i,12c,14b,28a,30], for example, $[\text{Mn}_6((\text{CH}_3)_3\text{CCO}_2)_8(\text{tmp})_2(\text{py})_2]$ ($\text{H}_3\text{tmp} = (1,1,1\text{-tris(hydroxymethyl)propane})$)^[30b], containing a core of $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_4]^{14+}$ rod- or ladder-like unit with four edge-sharing triangles; $[\text{Mn}^{\text{III}}_6\text{O}_2(\text{sao})_6(\text{O}_2\text{CH})_2(\text{CH}_3\text{OH})_4]$ ($\text{sao} = \text{salicylaldoxime}$)^[30f]

contains a nonplanar $[\text{Mn}^{\text{III}}_6(\text{O})_2(\text{OR})_2]^{12+}$ unit of two off-set, stacked $[\text{Mn}^{\text{III}}_3(\text{O}^{2-})]^{7+}$

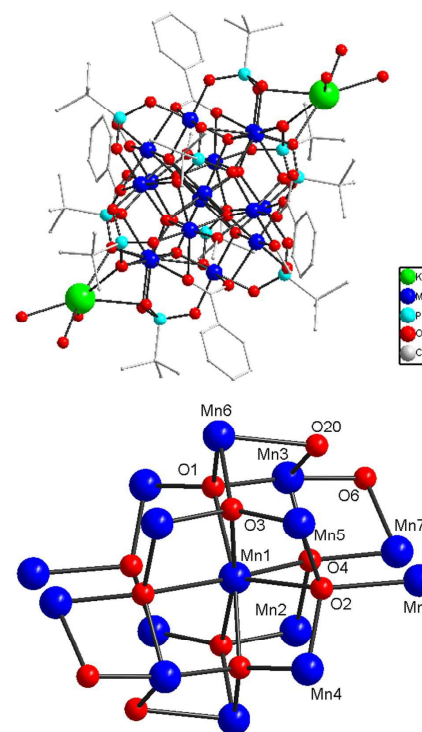


Figure 4. Molecular structure of cluster 4 (top); the core of cluster 4 (bottom). The noncoordinated solvent molecules and hydrogen atoms are omitted for clarity.

triangular subunits; $[\text{Mn}_6\text{O}_2(\text{O}_2\text{CPh})_8\text{L}_3]$ ($\text{L} = 1\text{-phenyl-3-(2-pyridyl)propane-1,3-dione}$)^[30k], with a $[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_3(\mu_4\text{-O})_2]^{11+}$ core, which comprises a central, distorted cubane like $[\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_2\text{O}_2(\text{OR})(\text{O}_2\text{CR})]$. Obviously, clusters 1 and 2 are completely different from that any previous structures reported.

The structure of cluster 3 is shown in Figure 3, and selected interatomic distances and angles are listed in Table S2. Cluster 3 crystallizes in the triclinic P-1 space group with C2v symmetry, and it is composed of two similar structural units of Mn_{13} with a little difference in the peripheral ligands. One unit of Mn_{13} can be described as the central Mn_1 , connected to Mn_2 , Mn_3 , Mn_6 and their symmetry-related partners by $\mu_4\text{-O}$ bridging ligands O1, O2, O4, forming a “four face-sharing defective cubane” unit $[\text{Mn}_7\text{O}_6]^{8+}$ core. Such core can be found in $[\text{Mn}_7]^{[31]}$, $[\text{Mn}_{13}]^{[32]}$, and $[\text{Mn}_{25}]^{[8g]}$ clusters. Mn_4 , Mn_5 and Mn_7 bridge to Mn_1 by O1, O2 and O4, respectively, and Mn_5 also connect to Mn_3 and Mn_6 through O5 and O23. The distance of $\text{Mn}_1\text{--O}_1$ is 2.230(3), $\text{Mn}_1\text{--O}_3$ is 2.273(4) Å and $\text{Mn}_1\text{--O}_4$ is 2.404(4) Å, the distances between metal centres range from 2.9924(14) Å to 3.1114(17) Å, with the metal centre bridged by a pair of $\mu_4\text{-O}$ groups having the shortest distances of 2.9924(14) Å ($\text{Mn}_2\cdots\text{Mn}_3$) and 3.0009(12) Å ($\text{Mn}_1\cdots\text{Mn}_6$). The other Mn_{13} unit is similar to the above described, so it is not repeated here. All $t\text{-BuPO}_3^{2-}$ ligands adopt two coordination modes: [4.211] and [3.111] in the two structural units and two $t\text{-BuPO}_3\text{H}_2$ ligands in one unit adopt binding mode [1.100] by

Harris notation. Peripheral ligation of cluster **3** is completed by H₂O and CH₃OH groups. All manganese ions are six-coordination in a distorted octahedron pyramid geometry by oxygen atoms, and the Mn^{III} ions display a Jahn-Teller (JT) distortion as expected for high-spin Mn^{III} (d⁴) in near-octahedral geometry. According to the BVS calculations, two central Mn atoms are in the oxidation state +2 and the others are in the oxidation state +3 (Table S4). It is worth mentioned that each unit Mn₁₃ of Mn₂₆ cluster is similar with the [Mn₁₃] in the literature.^[21] However, The ligand of reported Mn₁₃ is cyclohexanephosphonic acid and the peripheral ligation is completed by pyridine group.

The structure of cluster **4** is depicted in Figure 4 and selected interatomic distances and angles are listed in Table S3. According to the bond valence sum calculations, three of the manganese atoms (central Mn1 and two symmetrical Mn8 atoms) are in the oxidation state +2 and the others are in the oxidation state +3 (Table S5). Cluster **4** crystallizes in the monoclinic space group P2(1)/n, and the symmetric structure can be described as the central Mn1, connected to the surrounding manganese ions by μ_4 -O bridging ligands O1, O2, O3, O4. The MnO₆ central unit forms a distorted octahedron. Among them, O1 connects the central Mn1 to Mn4, Mn3, and Mn6; O3 connects the central Mn1 to Mn2, Mn5, and Mn6; O4 connects the central Mn1 to Mn3, Mn2, and Mn7. The Mn8 atoms link to the central Mn1, Mn4 and Mn5 by the μ_3 -O bridging ligand O2. The distance of Mn1–O1 is 2.18(2) Å, Mn1–O2 is 2.64(2) Å, Mn1–O3 is 2.32(2) Å, and Mn1–O4 is 2.511(19) Å. Two potassium ions bridge to the manganese ions through three μ -alkoxo groups of the *t*-BuPO₃²⁻ ligands, and the peripheral ligation is provided by three H₂O groups. The K⁺ is six coordinate with triangular prism geometry. Two benzoic acid ligands adopt η^2 : η^2 : μ_4 mode link to Mn2, Mn3, Mn4, Mn5, while the remaining two PhCOO⁻ groups join to Mn7 by the η^1 : η^0 : μ_1 mode. Ten *t*-BuPO₃²⁻ ligands in this cluster adopt four bridging modes: [6.222], [5.221], [4.211] and [3.111]. All manganese ions are six-coordination by oxygen atoms with octahedron geometries, and Mn^{III} ions show Jahn-Teller distortion as expected, giving rise to the elongation axis. It is noticed that the [Mn₁₅K₂] cluster is similar to the reported [Mn₁₅(μ_4 -O)₆(μ_3 -O)₂(μ_2 -CH₃O)₄(CH₃O)₂(C₄H₉PO₃)₁₀ (4-dmbpy)₂.6MeOH (C₄H₉PO₃H₂ = *tert*-butylphosphonic acid, 4-dmbpy = 4,4'-dimethyl-2,2'-dipyridyl)]^[17b], the difference is the external part of the cluster Mn₁₅ is completed by two CH₃O and 4-dmbpy ligands, but the peripheral ligation is completed by four PhCOO⁻ and eight H₂O groups in cluster **4**. Moreover, two potassium ions in cluster **4** bridge to the manganese ions through three μ -alkoxo groups to form a heptadecanuclear heterometallic cluster other than a homometallic [Mn₁₅]^[17b].

TGA

To examine the thermal stability of the heterometallic frameworks, TGA of **1–4** were examined in air atmosphere from 30 to 800 °C (Figure S1). Their TG curves show the lattice and coordination water molecules and methanol molecules were gradually lost in the temperature range of 30–190 °C for **1** (calcd/found: 11.07/10.96%), 30–220 °C for **2** (calcd/found:

14.45/14.80%), 30–210 °C for **3** (calcd/found: 8.07/8.03%), and 30–340 °C for **4** (calcd/found: 7.74/7.82%). Then the other ligands started to lost and the structures gradually decompose with increased temperatures.

Magnetic properties

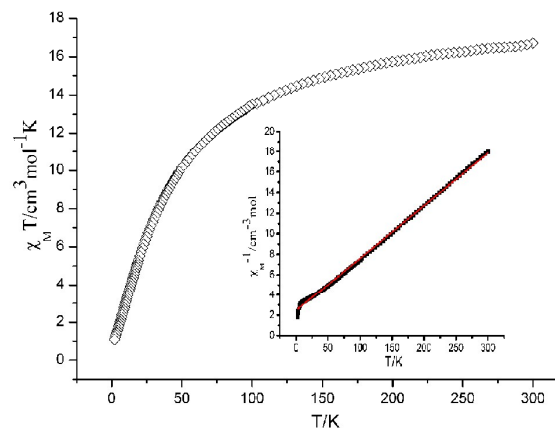


Figure 5 Temperature dependence $\chi_M T$ values for cluster **1**. The inset is the curve of χ_M^{-1} vs. T , and the solid line corresponds to the best-fit curve.

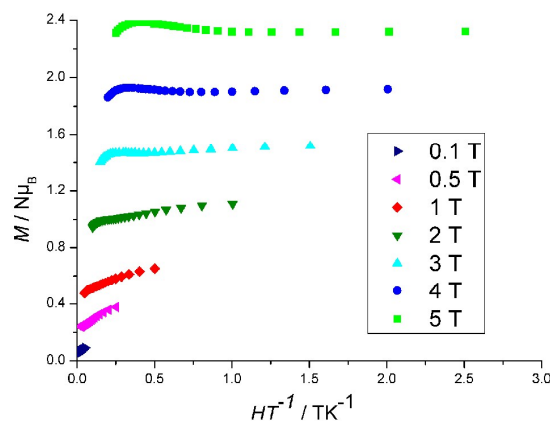


Figure 6 Plots of $M/N\mu_B$ vs H/T for cluster **1** at the indicated applied fields

The solid-state, variable temperature direct-current (DC) susceptibility magnetic studies carried out on clusters **1–4** were collected on a PPMS-9T superconducting magnetometer under a field of 0.1 T in the variable-temperature (2.0–300 K). The resulting plots of $\chi_M T$ versus T and χ_M^{-1} versus T are depicted in Figures 5, 8, 9, respectively. The structures of clusters **1** and **2** are similar, so only the magnetic data of **1** is collected. As shown in the figure 5, upon lowering the temperature, the $\chi_M T$ decreases smoothly from the value of 16.71 cm³ mol⁻¹ K (300 K) to 13.10 cm³ mol⁻¹ K (92 K), and then the value falls sharply to 1.09 cm³ mol⁻¹ K (2 K). This result reveals the overall intramolecular antiferromagnetic with the cluster and a ground state $S = 0$. The $\chi_M T$ value (16.71 cm³ mol⁻¹ K) at room temperature is smaller than that of 18.00 cm³ mol⁻¹ K expected for six independent Mn^{III} ions with $S = 2$. The temperature dependence of reciprocal susceptibility data above 20 K obeys the Curie-

Weiss law (the inset of Figure 6), and the derived Weiss constant (θ) of -48.23 K and Curie constant (C) of 19.51 cm³K mol⁻¹ are obtained, where the negative θ value suggests the antiferromagnetic interactions between Mn^{III} ions within the Mn₆ cluster. Magnetization data M for complex **1** were collected in the temperature range 2–10 K and the DC magnetic field range 0.1–5 T (Figure 6), but no satisfactory fit of the data was obtained.

The alternating-current (AC) magnetic susceptibility of cluster **1** was measured on a Quantum Design MPMS-XL magnetometer. This magnetometer works in an oscillating AC field of 3.0 G and AC frequencies ranging from 511 to 2311 Hz without using DC field. The in-phase signal $\chi'_M T$ and out-of-phase signal χ''_M vs. T plots are shown in Figure S2. Both the $\chi'_M T$ and χ''_M signals are not frequency-dependent, indicating cluster **1** is not a single molecule magnetic (SMM). In view of the structural core of clusters **3–4** resemble the reported [Mn13]^[21], [Mn15]^[17b], we do not carry out their AC susceptibility magnetic studies.

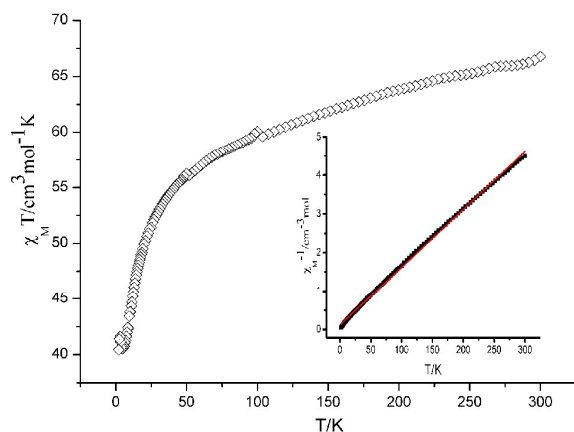


Figure 7 Temperature dependence $\chi_M T$ values for cluster **3**. The inset is the curve of χ_M^{-1} vs. T , and the solid line corresponds to the best-fit curve.

As for cluster **3**, the $\chi_M T$ value 66.79 cm³mol⁻¹K at 300 K is much smaller than that expected for a non-interacting 24Mn^{III}–2Mn^{II} systems (80.78 cm³mol⁻¹K for $g = 2$). Figure 8 shows the $\chi_M T$ value gradually decreases to 40.45 cm³mol⁻¹K upon cooling to 2 K. This behaviour indicates the presence of dominating and strong antiferromagnetic exchange interactions within **3**. As shown in the inset of figure 8, the χ_M^{-1} data above 20 K obey the Curie-Weiss law with the derived Weiss constant (θ) of -7.90 K and Curie constant (C) of 66.75 cm³mol⁻¹K, which reveals the presence of antiferromagnetic coupling between the Mn (II/III) ions within Mn₂₆ cluster.

The $\chi_M T$ value at 300 K is 37.53 cm³mol⁻¹K for **4**, is smaller than that of 49.01 cm³mol⁻¹K expected for twelve independent Mn^{III} ions with $S = 2$ and three Mn^{II} ions with $S = 5/2$. Upon cooling, the value of $\chi_M T$ gradually decreases to 24.69 cm³mol⁻¹K at 2 K (Figure 9). This result reveals the overall intramolecular antiferromagnetic character of the system. As shown in the inset of figure 9, the temperature dependence of reciprocal susceptibility χ_M^{-1} data follow the Curie-Weiss law with the Weiss constant (θ) of -10.61 K and Curie constant (C)

of 26.70 cm³K mol⁻¹ are obtained. Cluster **4** has a negative θ value, also suggesting the antiferromagnetic interactions between the Mn ions within the Mn₁₅ cluster.

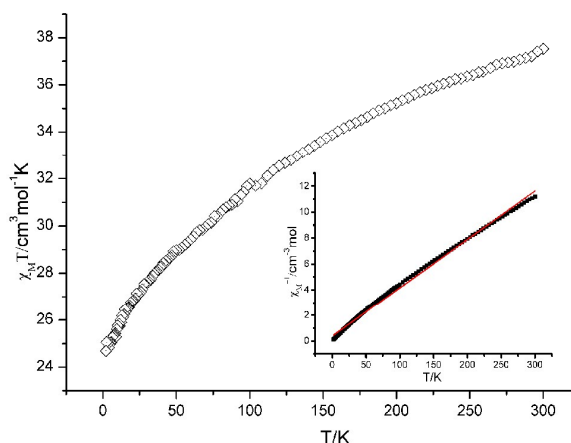


Figure 8 Temperature dependence $\chi_M T$ values for cluster **4**. The inset is the curve of χ_M^{-1} vs. T , and the solid line corresponds to the best-fit curve.

Conclusions

By the synthetic strategy of shifting different manganese sources in the same reaction system: $t\text{-BuPO}_3\text{H}_2\text{--Mn}^{2+}\text{--RCOOH}$, we have successfully prepared and characterized three different types of manganese phosphonate clusters **1–4**. The hexanuclear cluster containing a cage core with the halide ion (Cl⁻, Br⁻) in the center of the cage, and this kind of structural assembly is unprecedented for manganese clusters. The magnetic properties of these clusters show antiferromagnetic couplings among the Mn ions. The experimental finding suggests the manganese sources are as important as the other reaction conditions including alkaline reagents, phosphoric acid, as well as ancillary ligands, providing an important addition to the study of manganese phosphonate chemistry. The other transition metal phosphonate clusters with interesting structures will be further exploited in our future work.

Acknowledgements

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A table of contents entry:

Four manganese clusters containing tert-butylphosphonate ligand with diverse structures have been synthesized and characterized.

