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Self-assembly of two high-nuclearity manganese calixarene-phosphonate clusters: diamond-Like Mn$_{16}$ and drum-Like Mn$_{14}$

Kongzhao Su,[ab] Feilong Jiang,[a] Jinjie Qian,[ab] Jie Pan,[ab] Jiandong Pang,[ab] Xiuyan Wan,[ab] Falu Hu[ab] and Maochun Hong*[a]

Two novel high-nuclearity manganese clusters, [Mn$_{14}$(BSC4A)$_3$(tBuPO$_3$)$_6$(μ_4-OH)$_3$Cl(H$_2$O)(CH$_3$OH)]•1.5CH$_3$OH (**1**) and [Mn$_{16}$(BSC4A)$_3$(PhPO$_3$)$_7$(HPO$_4$)(μ_4-OH)$_3$Cl(H$_2$O)(CH$_3$OH)$_4$]•4.5CH$_3$OH (**2**) (H$_4$BSC4A = *p-tert*-butylsulfonylcalix[4]arene; tBuPO$_3$H$_2$ = tert-
10 butylphosphonic acid; PhPO$_3$H$_2$ = phenylphosphonic acid) have been solvothermally obtained and structurally characterized. Crystal structural analyses reveal that the phosphonate ligands have a large influence on the structures of the polynuclear manganese clusters: complex **1** possesses a drum-like Mn$^{II}_{14}$ core, which is constructed by three Mn$_4$-BSC4A molecular building blocks (MBBs) and six tBuPO$_3^{2-}$ ligands and capped by two Mn^{II} ions; while complex **2** has a diamond-like Mn$^{II}_{16}$ core, which
15 also consists of three Mn$_4$-BSC4A MBBs, but connected by seven PhPO$_3^{2-}$ linkers and a tetrahedral Mn$_4$ cluster housing a phosphate anion generated *in situ*. To the best of our knowledge, complex **2** gives the first calixarene-based cluster linked by both organic phosphonate and inorganic phosphate ligands, and also presents the highest nuclearity manganese complex with H$_4$BSC4A ligand to date. Magnetic measurements suggest the presence of antiferromagnetic interactions between the adjacent Mn^{II} spin
20 carriers for both complexes.

Introduction

The exploration of polynuclear transition metal clusters is currently a fertile topic of research, not only because of their architectural beauty[1] but also because of their immense
25 technological applications in molecular magnet,[2] catalysts,[3] optics[4] and so on.[5] Numerous transition metal clusters with different nuclearities, distinct geometries and interesting properties have been obtained utilizing multidentate ligands through hydro(solvo)thermal conditions, which may lead to some
30 unexpected architectures induced by *in situ* generated ligands.[6] *p-Tert*-butylsulfonylcalix[4]arene (H$_4$BSC4A, Scheme 1), a calixarene derivative possessing four lower-rim phenolic oxygen atoms and eight sulfonyl oxygen atoms, could be an ideal choice for the construction of polymetallic compounds.[7] Moreover, it has
35 been found that one H$_4$BSC4A molecule tends to coordinate to three or four divalent transition metal (TM) ions to form a shuttlecock-like TM$_{3/4}$-BSC4A molecular building block (MBB), which can be further bridged by different linkers into polynuclear entities. For example, two novel barrel-shaped Co$_{16}$ containers
40 built from four Co$_4$-BSC4A MBBs and eight dicarboxylate ligands,[8] a novel nest-like C_4-symmetric Co$_{24}$ metallamacrocycle constructed by eight Co$_3$-BSC4A molecular building blocks (MBBs) and six 1,2,4-triazolate ligands,[9] several octahedral M$_{24}$ nanocages (M = Co, Ni) with six M$_4$-BSC4A MBBs and twelve
45 dicarboxylates or eight tricarboxylates have been reported in
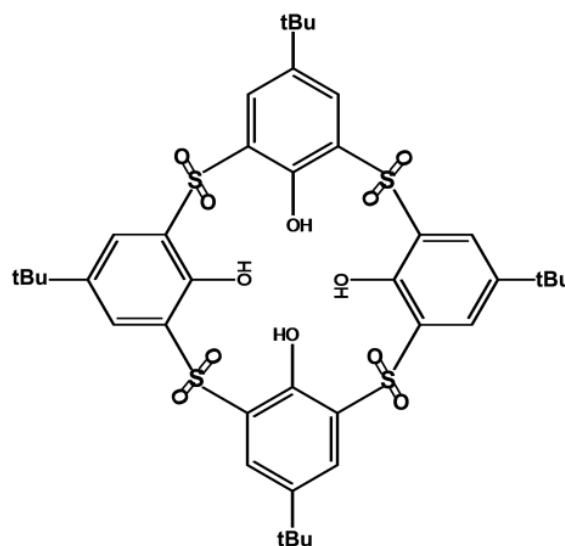
Scheme 1. *p-Tert*-butylsulfonylcalix[4]arene (H$_4$BSC4A)

recent years.[10] In addition, its analogs *p-tert*-butylcalix[4]arene (H$_4$BC4A) and *p-tert*-butylthiacalix[4]arene (H$_4$BTC4A) have
50 also been widely utilized in the syntheses of polymetallic compounds.[11]

On the other hand, phosphonate ligands possess different anionic forms and can adopt various coordination modes to bind to different metal ions.[12] In the past few years, a number of
55 groups have been utilizing phosphonate ligands with preformed

cages/clusters or pyrazoles, 2-chloro-6-hydroxypyridine, antimonite and carboxylate as co-ligands to make new polymetallic complexes.[13]

Our group has been focused on preparing new calixarene-based polynuclear compounds with fascinating structures and interesting physical properties.[14] In our recent work, we have isolated some calix[4]arene-based high-nuclearity complexes with interesting architectures and properties by the introduction of phosphonate/phosphate as co-ligands. For example, we have synthesized eight thiacalix[4]arene-based high-nuclearity TM_{4n} nanocages (TM = Co, Ni; n=2-6) constructed by bridging TM_4-calix[4]arene MBBs with phosphate/phosphonate ligands,[15] two large alkali-metal templated Na_2Co_{24} and KCo_{24} clusters constructed from six TM_4-thiacalix[4]arene MBBs and six phosphate linkers,[16] and a tri-capped trigonal prismatic Co_9 clusters with spin-glass behavior based on calix[4]arene and phosphonate ligands.[17] As an extension of our work, we have tried to expand the mixed calix[4]arene-phosphonate system using other transition metal salts. Fortunately, we have successfully obtained two new calix[4]arene-based manganese(II) clusters having the general molecular formula of $[Mn^{II}_{14}(BSC4A)_3(tBuPO_3)_6(\mu_4\text{-}OH)_3Cl(H_2O)(CH_3OH)]\cdot1.5CH_3OH$ (**1**) and $[Mn^{II}_{16}(BSC4A)_3(PhPO_3)_7(HPO_4)(\mu_4\text{-}OH)_3Cl(H_2O)(CH_3OH)_4]\cdot4.5CH_3OH$ (**2**) ($tBuPO_3H_2$ = tert-butylphosphonic acid; $PhPO_3H_2$ = phenylphosphonic acid). Single-crystal X-ray diffraction analyses reveal that the phosphonate ligands have a significant influence on the structure of the polynuclear manganese (II) compounds. Although both complexes contain three Mn4-BSC4A molecular building blocks MBBs (Figure 1), they are bridged by different numbers of manganese cations, different kinds and numbers of phosphonate ligands as well as other auxiliary ligands. In fact, the structure of **1** possesses a drum-like Mn^{II}_{14} core, whereas **2** a diamond-like Mn^{II}_{16} core. Bond distances, bond valence sum (BVS) calculations and charge balance authenticate that all manganese centers in both complexes are at +2 oxidation states.[18] To the best of our knowledge, there are only three tetranuclear Mn4 clusters based on H4BSC4A in the literature, thus **2** presents the highest nuclearity manganese complex with H4BSC4A ligand so far.[19] In this work, the syntheses, crystal structures and magnetic properties of complexes **1** and **2** were studied.
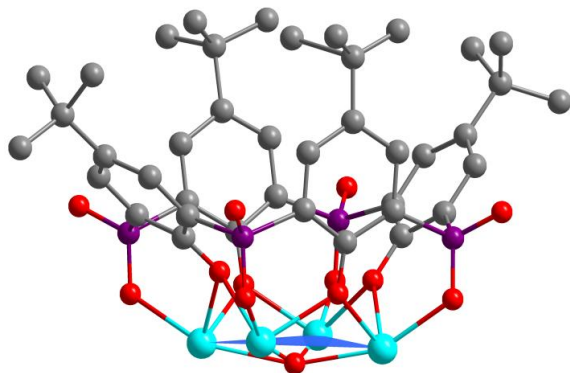

Figure 1. Shuttlecock-like MBB of Mn4-BSC4A, whose base is capped by a μ_4-hydroxide anion.

Experimental section

General Remarks. The H4BSC4A ligand was synthesized as previously reported.[20] All manipulations were performed under aerobic conditions utilizing chemical materials purchased from commercial sources and without further purification. The (C, H, N) elemental analyses were performed using a German Elementary Varil EL III instrument. Thermogravimetric analysis (TGA) curves were carried out on a NETZSCH STA 449C thermal analyzer in the temperature range of 25–900 ℃ in a nitrogen stream with a heating rate of 10 ℃ min^{-1}. The powder X-ray diffraction (PXRD) data were collected by a RIGAKU-DMAX2500 X-ray diffractometer using Cu Kα radiation (λ = 0.154 nm) at room temperature. Magnetic susceptibility measurements were measured with a Quantum Design PPMS-9T and MPMS-XL magnetometer. The experimental magnetic data were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

Synthesis of Complex 1. A mixture of H4BSC4A (0.1 mmol, 85 mg), $MnCl_2\cdot4H_2O$ (0.4 mmol, 80 mg), $tBuPO_3H_2$ (0.1 mmol, 14 mg) and 10mL CH_3OH was sealed in a 25 mL Teflon-lined bomb at 130 ℃ for 72 h. Eventually, the mixture was cooled down slowly to room temperature for 24 h, after which colorless block-shaped crystals of **1** were isolated by filtration, washed with CH_3OH and air dried (58% yield based on H4BSC4A ligand). Elemental analysis (%) for $C_{145}H_{177}O_{59}P_6S_{12}ClMn_{14}$: calcd: C, 41.08; H, 4.20; found (after dried in vacuum): C, 40.66; H, 4.13. The phase purity of the sample was determined by PXRD (Figure S3, in the Supporting Information).

Synthesis of Complex 2. Complex **2** was obtained in a procedure similar to that of **1**, except that $PhPO_3H_2$ (0.1 mmol, 16 mg) was used instead of $tBuPO_3H_2$ (0.1 mmol, 14 mg). Yield 76% based on H4BSC4A ligand. Elemental analysis (%) for $C_{166}H_{189}O_{69}P_8S_{12}ClMn_{16}$: calcd: C, 41.23; H, 3.94; found (after dried in vacuum): C, 42.06; H, 3.87. The phase purity of the sample was determined by PXRD (Figure S4, in the Supporting Information).

X-ray Crystallography. Data collection for **1** was performed on a SuperNova diffractometer at 100 K with graphite-monochromated Mo-Kα (λ = 0.71073 Å), while data of **2** was collected using a Rigaku Saturn 70 CCD diffractometer at 293 K with graphite-monochromated Mo-Kα (λ = 0.71073 Å). Crystallographic Data and Structure Refinement for compounds **1** and **2** were summarized in Table 1. Data were corrected for absorption using the *CrystalClear* program.[21] Structure solution by direct methods and full-matrix least-squares refinement on F^2 were solved by using *SHELXTL*-97 program package.[22] All the non-hydrogen atoms were refined anisotropically except some badly disordered carbon atoms of tert-butyl groups. Organic hydrogen atoms of the ligands were placed in calculated positions and refined isotropically with fixed thermal factors. Moreover, diffuse electron density together with highly disordered MeOH molecules of crystallization could not be generated and were not included for both structures, thus the crystal structures were treated by the "SQUEEZE" method, a part of the PLATON package of crystallographic software.[23] This had dramatically improved the agreement indices. Moreover, the high R_1 and wR_2 factor for both title complexes might be due to the weak crystal diffractions and the disorder of the tert-butyl groups. Crystallographic details for both compounds are available in the supporting information in CIF format.

Table 1. Crystallographic Data and Structure Refinement for Complexes 1 and 2

Complex	1	2
formula	$C_{145}H_{177}O_{59}P_6$ $S_{12}ClMn_{14}$	$C_{166}H_{189}O_{69}P_8$ $S_{12}ClMn_{16}$
M / g mol^{-1}	1.4225	1.4528
T / K	100	293
Crystal system	monoclinic	orthorhombic
Space group	P21/c	Pnma
a / Å	18.7857(3)	34.378(4)
b / Å	39.0027(6)	28.140(4)
c / Å	27.3636(4)	22.849(3)
α (°)	90.00	90
β (°)	99.2080(10)	90
γ (°)	90.00	90
V / Å^3	19790.8(5)	22104(5)
Z	4	4
μ (mm^{-1})	1.122	1.139
Data measured	101744	144413
Ind. reflns	34809	20856
Parameters	2183	1313
GOF on F^2	1.050	1.086
R$_1$[a] [I ›2 (I)]	0.0561	0.0709
wR$_2$[b]	0.1335	0.1987
CCDC number	1046923	1046924

[a]$R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$. [b]$wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/ \sum[w(F_o^2)^2]\}^{1/2}$

Results and Discussion

Crystal structures. Solvothermal treatment of H$_4$BSC4A with tBuPO$_3$H in methanol solution affords colorless single crystals of **1**. X-ray data diffraction analysis reveals that complex **1** crystallizes in the monoclinic system with space group *P21/c* and has a tetradecanuclear Mn$^{II}_{14}$ cluster. As can be seen from Figure 2, there are three fully deprotonated BSC4A^{4-} ligands, each of which coordinates to four Mn^{II} ions by its lower-rim phenoxy oxygen and bridge sulfur oxygen atoms forming a shuttlecock-like Mn$_4$-BSC4A MBB, whose bottom is capped by one μ_4-hydroxide anion. The bottoms of the Mn$_4$-BSC4A MBBs are linked together through the oxygen atoms from six different tBuPO$_3^{2-}$ ligands to form the body of a drum, whose "upper" and "lower" faces are each further capped by a Mn^{II} ion (Figure **3**). These 14 crystallographically independent Mn^{II} ions can be divided into three groups according to their coordination environments: (i) 12 Mn ions (Mn1-Mn12) from the abovementioned three Mn$_4$−BSC4A MBBs are coordinated by two phenoxo oxygen atoms along with one sulfonyl oxygen atom originating from one BSC4A^{4-} ligands, one μ_4-hydroxide anion, and two oxygen atoms from two independent tBuPO$_3^{2-}$ ligands to form a six-coordinated distort octahedral geometries; (ii) Mn13 is bounded by five oxygen atoms deriving from three different tBuPO$_3^{2-}$ ligands, one water oxygen and one chlorine to form a seven-coordinated pentagonal bipyramid geometry; (iii) while the rest Mn14 ion is coordinated by four oxygen atoms from three independent tBuPO$_3^{2-}$ ligands and one ligated MeOH molecule to form a five-coordinated square-pyramid geometry. Impressively, six tBuPO$_3^{2-}$ ligands coordinate to the Mn ions in two different chelating modes: three with [5.2$_{12}$2$_{34}$2$_{45}$] coordination mode, and the rest three with [5.221] fashion according to Harris notation (Scheme 1).[24] To the best of our knowledge, there are two
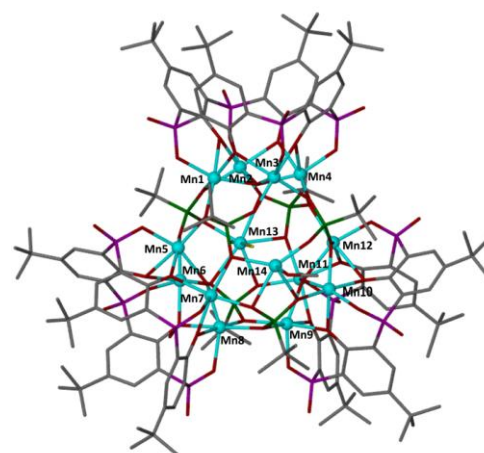

Figure 2. Molecular structure of complex **1**. The hydrogen atoms and isolated solvent molecules are omitted for clarity.
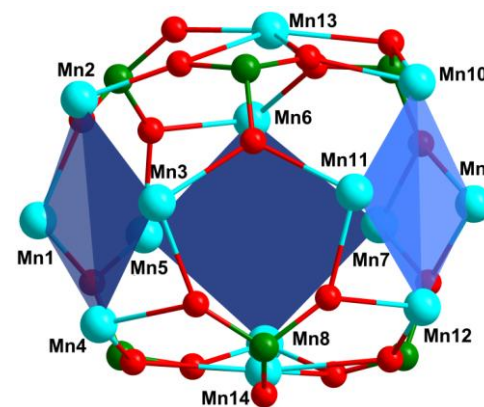

Figure 3. Core structure of complex **1**. Calix[4]arene ligands and tBu groups are omitted for clarity.

compounds supported by H$_4$BSC4A ligands with tetradecanuclear structures. One is constructed from two Co$_4$–BSC4A building blocks, two Co$_3$–BSC4A subunits and 12 bridging tetrazolate ligands,[7d] and the other one is a cationic cluster composed of three BSC4A^{4-} ligands and 14 Co^{II} ions and formed by two superposed planar, bodycentered, hexagonal cores by seven Co^{II} ions.[7e] However, they are different from complex **1** which possesses a drum-shaped Mn$^{II}_{14}$ core.
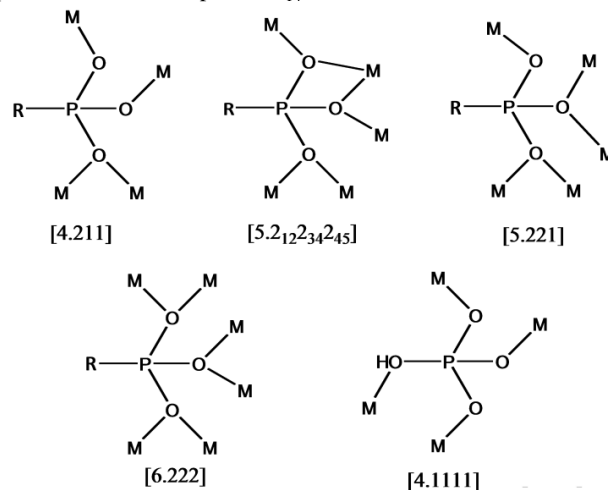
Scheme 1. Observed bonding modes of the phosphonate and phosphate ligands.

The phosphonate ligands have a pivotal influence on the final structure of title complexes. By replacing the tBuPO$_3$H ligand to PhPO$_3$H ligand in the similar reaction, complex **2** was obtained. It crystallizes in an orthorhombic cell with the space group *Pnma*,

5 and contains an unprecedented diamond-like Mn$^{II}_{16}$ core. As shown in Figure 4a, complex **2** is also constructed from three Mn$_4$−BSC4A MBBs to compare with **1**, but linked by seven PhPO$_3^{2-}$ ligands and one phosphate-based tetrahedral Mn$_4$ cluster. The "upper" part of the core is built by three Mn$_4$-BSC4A MBBs and

10 linked together through four different PhPO$_3^{2-}$ ligands, while the "lower" part is a tetrahedral Mn$_4$ cluster, which are bridged by three different PhPO$_3^{2-}$ ligands and one in situ generated HPO$_4^{2-}$ anion (Figure 5). Then the "upper" part and "lower" part are further linked by three different PhPO$_3^{2-}$ ligands to form a

15 diamond-like Mn$^{II}_{16}$ core. Unlike **1**, complex **2** has a crystallographic symmetry plane, so its asymmetric unit includes half of the formula and there are nine crystallographically independent manganese atoms (Mn1-Mn9) in this structure. Six Mn ions (Mn1-Mn6) from the Mn$_4$−BSC4A MBBs have the same

20 coordination environments to compare with those of **1**. The remaining three Mn ions are all six-coordinated and exhibit octahedral geometries, but they have different coordination environments. Specially, Mn7 is in O$_6$ environment with four oxygen atoms from two different PhPO$_3^{2-}$ ligands, one oxygen

25 from HPO$_4^{2-}$ anion and one water oxygen; Mn8 is in ClO$_5$ environment with two oxygen atoms from two different PhPO$_3^{2-}$ ligands, one oxygen from HPO$_4^{2-}$ anion, one chlorine anion and two MeOH molecules; Mn9 is in O$_6$ environment with four oxygen atoms from three different PhPO$_3^{2-}$ ligands, one oxygen

30 from HPO$_4^{2-}$ anion and one MeOH molecules (Figure 4b). Notably, seven PhPO$_3^{2-}$ anions adopt four different binding modes: (i) three ligands coordinate in a [6.222] manner; (ii) two adopt the [5.221] modes; (ii) one binds in a [5.2$_{12}$2$_{34}$2$_{45}$] fashion; (iv) while the remaining one coordinates in a [4.211] mode. It

35 should be note that the difference between the final structures of title complexes might arise from the unexpected *in situ* generated HPO$_4^{2-}$ anion. The HPO$_4^{2-}$ anion in this structure is generated from *in situ* reactions of PhPO$_3$H$_2$ molecule during the solvethermal conditions, which coordinates to four Mn centers in

40 a [4.1111] coordination mode (Scheme 1) to form a tetrahedral Mn$_4$ cluster and further to generate unexpected cluster structure. We note that this phosphate anion carries a hydrogen atom, because one of the distances between the phosphorus and oxygen atoms are considerably longer than the other three, which is in

45 agreement with the previously reported phosphate-based compounds.[25] To the best of our knowledge, complex **2** gives the first calixarene-based cluster linked by both organic phosphonate and inorganic phosphate ligands. This sheds some light into the design and construction of other calixarene-based high-nuclearity

50 compounds by utilizing both phosphonate and phosphate linkers. Although there have been several reports on calix[4]arene-based M$_{16}$ (M = Co, Ni) clusters, those clusters are squares constructed by four Co$_4$-calix[4]arene MBBs with eight in situ generated 5-methyltetrazolates or rigid 1,3-benzenedicarboxylates, this

55 unusual diamond-like Mn$_{16}$ architecture has not been reported heretofore.[10]
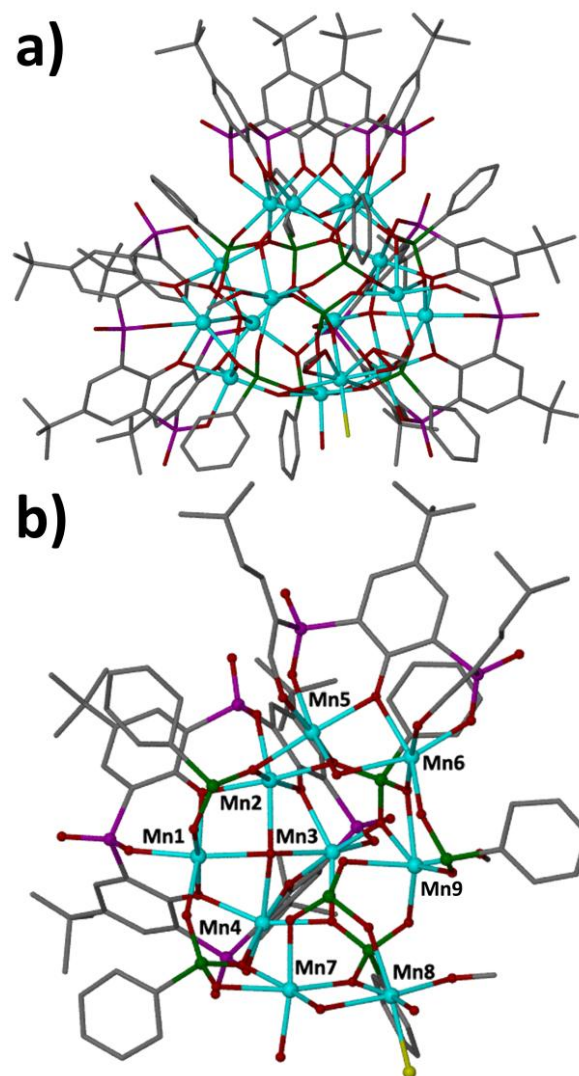

Figure 4. (a) Molecular structure of complex **2**. (b) X-ray asymmetric 60 unit of **2**. The hydrogen atoms and isolated solvent molecules are omitted for clarity.
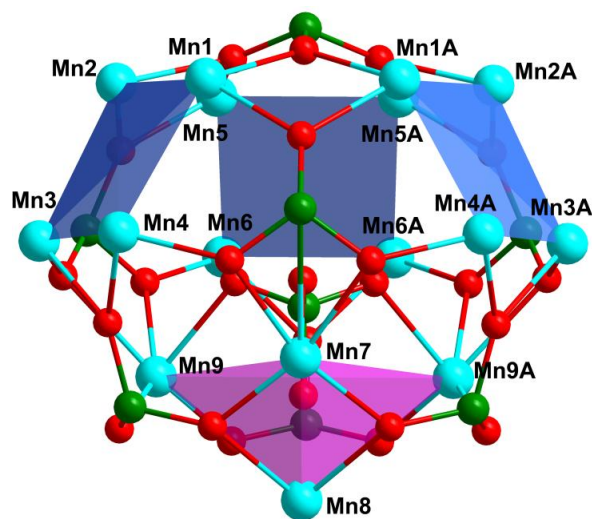

Figure 5. Core structure of complex **2**. Calix[4]arene ligands and phenyl groups are omitted for clarity. Symmetry code: A x, 3/2-y, z.

Magnetic studies. The variable-temperature dependence of solid state direct current (dc) magnetic susceptibilities were collected on the polycrystalline samples of **1** and **2** in the temperature range of 2-300 K under a field of 1 kOe. These results are plotted as the $\chi_m T$ products (χ_m is molar magnetic susceptibility) versus temperature in Figures 6 and 7. The $\chi_m T$ values at 300 K are 48.92 and 54.81 cm^3 K mol^{-1} for **1** and **2**, which are smaller than the expected values of 61.25 and 70 cm^3 K mol^{-1} for 14 and 16 non-interacting high-spin Mn^{II} spin carrier (S = 5/2, g = 2), respectively.[26] As the temperature is decreased, the $\chi_m T$ values continuously decrease to 2.07 and 5.06 cm^3 K mol^{-1} until the lowest temperature 2 K for **1** and **2**, respectively. The χ_m^{-1} data above 50 K obey the Curie–Weiss Law with Curie constants (C) = 62.38 and 70.37 and Weiss constants (θ) = -83.72 and -85.96 cm^3 K mol^{-1} for **1** and **2**, respectively. The negative Weiss constants, together with the trend of $\chi_m T$ vs T plots, reveal the presence of strong antiferromagnetic interaction between Mn^{II} ions. However, the coupling parameters (J) of both title clusters cannot be carried out owing to the complexities of the structures.
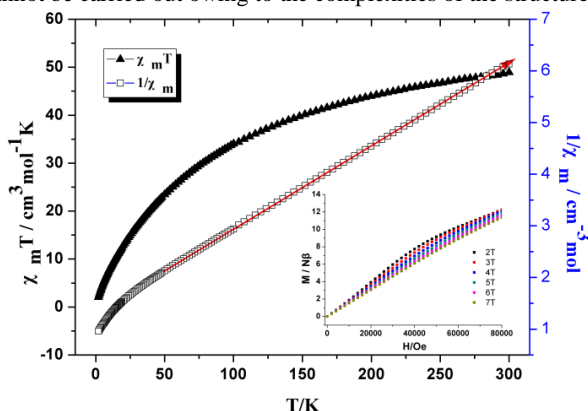

Figure 6. Temperature dependence of $\chi_m T$ measured in a 1 kOe field. The solid lines are the best fitting to the Curie-Weiss Law. Magnetization curves (inset graphs) measured at 2−7 K for **1**.
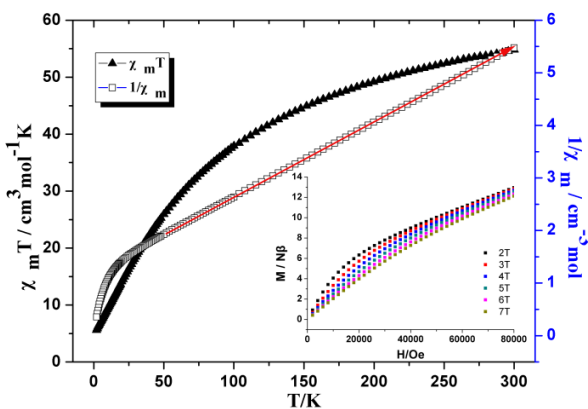

Figure 7. Temperature dependence of $\chi_m T$ measured in a 1 kOe field. The solid lines are the best fitting to the Curie-Weiss Law. Magnetization curves (inset graphs) measured at 2−7 K for **2**.

The field dependence of magnetization (M) versus field (H) data for **1** and **2** from 2 to 7 K are investigated with the applied magnetic field H in the range 0–80 kOe (inset of Figures 6 and 7, respectively). The magnetization of **1** and **2** continuously increases almost linearly and the magnetization value at the highest field (80 kOe and 2 K) is 12.24 and 12.95 Nβ for complexes **1** and **2** respectively, which are far from the saturation sum values of 14 and 16 Mn^{II} ions. The temperature-dependent alternating current (ac) susceptibility studies of **2** are also carried out between 20 and 2 K with and without applied dc field, but no peaks for the out-of-phase component is observed (Figure S1, in the Supporting Information). Moreover, no obvious hysteresis loop is observed for **2** at 2 K (Figure S2, in the Supporting Information). All these results reveal neither long-range ordering nor single-molecule magnet behavior above 2 K for **2**.

Conclusion

In conclusion, we have synthesized two novel polynuclear manganese clusters based on H$_4$BSC4A and phosphonate ligands. We found that the phosphonate ligands have an important influence on the final structures of title complexes. When tBuPO$_3$H$_2$ was utilized, a tetradecanuclear drum-like Mn$^{II}_{14}$ cluster (**1**) was obtained. By variation of the phosphonic acid from tBuPO$_3$H$_2$ to PhPO$_3$H$_2$, a hexadecanuclear diamond-like Mn$^{II}_{16}$ cluster (**2**) was synthesized. To the best of our knowledge, complex **2** presents the highest nuclearity manganese complex supported by H$_4$BSC4A ligand and also gives the first calixarene-based cluster linked by both organic phosphonate and inorganic phosphate ligands. Magnetic measurements suggest the presence of antiferromagnetic interactions between the adjacent Mn^{II} centers. Our future studies will focus on polynuclear lanthanide compounds of mixed calixarene-phosphonate ligands.

Acknowledgment

Notes and references

^{a}State Key Laboratory of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, China
^{b}University of the Chinese Academy of Sciences, Beijing, 100049, China

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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