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Dodecanuclear Manganese(III) Phosphonates with Cage Structures

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Treatments of $Mn(O_2CR)_2$ (R = Me, Ph) with NBu_4MnO_4 in CH_3CN or CH_3CN/CH_2Cl_2 in the presence of acetic acid, δ^1-cyclohexenephosphonic acid ($C_6H_9PO_3H_2$), and 2,2′-bipyridine or 1,10-phenanthroline result in three novel dodecamanganese(III) clusters $[Mn_{12}O_8(O_2CMe)_6(O_3PC_6H_9)_7(bipy)_3]$ (**1**), $[Mn_{12}O_8(O_2CPh)_6(O_3PC_6H_9)_7(bipy)_3]$ (**2**), and $[Mn_{12}O_8(O_2CPh)_6(O_3PC_6H_9)_7(phen)_3]$ (**3**). They have a similar Mn_{12} core of $[Mn^{III}_{12}(\mu_4\text{-}O)_3(\mu_3\text{-}O)_5(\mu\text{-}O_3P)_3]$ with a new type of topologic structure. Solid-state dc magnetic susceptibility measurements of complexes **1**–**3** reveal that dominant antiferromagnetic interactions are propagated between the magnetic centers. The ac magnetic measurements suggest an $S = 2$ ground state for compounds **1** and **3** and an $S = 3$ ground state for compound **2**.

Introduction

Current interests in the chemistry of higher oxidation-state molecule compounds of manganese draw from their utility as models for the photosynthetic water oxidation centers[1] and their potential as single molecule magnets (SMMs).[2] Over the past 10 years, a number of high-nuclearity manganese clusters have been reported.[3−16] Among these, the $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ ($Mn_{12}-O_2CR$) family, possessing a $[Mn_{12}(\mu_3\text{-}O)_{12}]$ core comprising a central $[Mn^{IV}{}_4O_4]^{8+}$ cubane held within a nonplanar ring of eight Mn^{III} ions by eight $\mu_3\text{-}O^{2-}$ ions, is the most thoroughly studied members which exhibit SMM behavior at the highest temperatures.[3] Other Mn_{12} clusters with different structure types include cage complex $[Mn_{12}O_8X_4(O_2CPh)_8L_6]$ [X = Cl, Br; L = 1-(hydroxymethyl)pyridine (hmpH), 2-(hydroxyethyl)pyri-

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dine (hepH)],[4] ladderlike complex $[Mn_{12}O_4(OH)_2(O_2CPh)_{12}(thme)_4(py)_2]$ [H_3thme = 1,1,1-tris(hydroxymethyl)ethane],[5] and wheel-shaped complex $[Mn_{12}(O_2CCH_3)_{14}L_4]$ [L = *N*-methyldiethanol (mdea), *N*-ethyldiethanol (edea)].[6] Typical ligands for assembling these cluster compounds are carboxylates or alkoxides.

Phosphonates (RPO_3^{2-}) are powerful ligands that can link metal ions through their three phosphonate oxygen atoms. A number of metal phosphonate compounds with polymeric structures have been prepared due to their potential applications in ion exchange, sorption, catalysis, magnetism, etc.[17] Cluster compounds featuring phosphonate ligands, however, are rare. As far as we are aware, there is only one manganese phosphonate cage complex $[Mn_6O_2(O_3PPh)_2(O_2PHPh)_2(O_2CPh)_8(py)]$[18] that has been structurally characterized, although several other transition metal phosphonate clusters including copper,[19] cobalt,[18] iron,[20] vanadium,[21] and zinc[22] cages have been described. A few mixed-valent dodecamanganese(III,-IV) complexes containing phosphinate ligands were also reported,[23] which possess cores similar to those of the $Mn_{12}-O_2CR$ family. In recent years, we have been interested in both the structures and magnetic properties of transition metal phosphonates. A series of low-dimensional polymeric compounds were prepared via the hydrothermal technique which show interesting magnetic properties.[24] Herein we report three dodecamanganese(III) complexes, namely, $[Mn_{12}O_8(O_2CMe)_6(O_3PC_6H_9)_7(bipy)_3]$ (**1**), $[Mn_{12}O_8(O_2CPh)_6(O_3PC_6H_9)_7(bipy)_3]$ (**2**), and $[Mn_{12}O_8(O_2CPh)_6(O_3PC_6H_9)_7(phen)_3]$ (**3**), with a new type of cage structure, prepared by solution reactions.

Experimental Section

Materials and Methods. The δ^1-cyclohexenephosphonic acid ($C_6H_9PO_3H_2$),[25] $Mn(PhCO_2)_2\cdot 2H_2O$,[26] and NBu_4MnO_4[27] were synthesized according to the literature. All the other starting materials were of reagent grade and were obtained from commercial sources without further purification. Elemental analyses were performed in a PE240C elemental analyzer. The infrared spectra were recorded on a VECTOR 22 spectrometer with pressed KBr pellets. Variable-temperature magnetic susceptibility data were obtained on polycrystalline samples (16.7 mg for **1**, 21.23 mg for **2**, and 13.85 mg for **3**) from 1.8 to 300 K in a magnetic field of 2 kOe, using a Quantum Design MPMS-XL7 SQUID magnetometer. The data were corrected for the diamagnetic contributions of both the sample holder and the compound obtained from Pascal's constants.[28]

Synthesis of $[Mn_{12}O_8(O_2CMe)_6(O_3PC_6H_9)_7(bipy)_3]$, 1. NBu_4MnO_4 (0.091 g, 0.25 mmol) was added in small portions to a slurry of $Mn(MeCO_2)_2\cdot 4H_2O$ (0.245 g, 1.0 mmol) in CH_3COOH (0.090 g, 0.15 mmol) and 15 mL of CH_3CN, to which $C_6H_9PO_3H_2$ (0.081 g, 0.5 mmol) and 2,2′-bipyridine (0.078 g, 0.5 mmol) in 2 mL of CH_3OH was added. After the mixture was stirred for 10 h, the deep-brown filtrate was allowed to evaporate slowly in air. Black crystals of compound **1**·7.5H_2O appeared after a few days. Yield: ca. 52% based on Mn. Anal. Calcd for **1**·7.5H_2O ($C_{84}H_{105}N_6O_{41}P_7Mn_{12}\cdot 7.5H_2O$): C, 35.17; H, 4.19; N, 2.93. Found: C, 35.80; H, 3.90; N, 3.17. IR (KBr, cm^{-1}): 3433 br, 3109 w, 2930 s, 2860 w, 1639 m, 1572 s, 1499 w, 1447 m, 1406 s, 1339 m, 1269 w, 1244 w, 1122 s, 1089 s, 1032 s, 964 s, 775 m, 733 m, 662 m, 633 s, 609 s, 527 m, 455 w, 417 w.

Synthesis of $[Mn_{12}O_8(O_2CPh)_6(O_3PC_6H_9)_7(bipy)_3]$, 2. This was prepared by a procedure analogous to that for **1** but using $Mn(PhCO_2)_2\cdot 2H_2O$ instead of $Mn(MeCO_2)_2\cdot 4H_2O$ as the starting material and in a CH_3CN/CH_2Cl_2 solution. Yield: ca. 25% based on Mn. Anal. Calcd for **2**·5.2H_2O ($C_{114}H_{117}N_6O_{41}P_7Mn_{12}\cdot 5.2H_2O$): C, 42.79; H, 3.99; N, 2.63. Found: C, 42.24; H, 4.08; N, 2.48. IR (KBr, cm^{-1}): 3414 br, 3109 w, 3069 m, 3024 w, 2932 s, 2862 m, 1639 m, 1599 s, 1562 s, 1495 w, 1447 m, 1393 s, 1317 w, 1265 w, 1177 w, 1120 s, 1089 s, 1026 s, 962 s, 847 w, 771 m, 719 s, 631 m, 609 s, 548 m, 509 m, 453 w, 415 w.

Synthesis of $[Mn_{12}O_8(O_2CPh)_6(O_3PC_6H_9)_7(phen)_3]$, 3. This was prepared by a procedure analogous to that for **2** except that the 1,10-phenanthroline instead of 2,2′-bipyridine was used as the coligand. Yield: ca. 33% based on Mn. Anal. Calcd for **3**·10H_2O ($C_{120}H_{117}N_6O_{41}P_7Mn_{12}\cdot 10H_2O$): C, 42.88; H, 4.29; N, 2.50. Found: C, 42.21; H, 4.24; N, 2.10. IR (KBr, cm^{-1}): 3425 br, 3057 w, 2932 s, 2862 m, 1639 m, 1597 s, 1560 s, 1520 m, 1493 w, 1390 s, 1317 w, 1269 w, 1227 w, 1177 w, 1122 s, 1089 s, 1026 s, 962 s, 850 w, 721 s, 677 m, 631 m, 609 s, 548 m, 432 w.

Crystallographic Studies. Single crystals of dimensions 0.30 × 0.20 × 0.10 mm for **1**, 0.20 × 0.15 × 0.15 mm for **2**, and 0.25 × 0.20 × 0.18 mm for **3** were used for data collections on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å) at room temperature. In all cases the selected crystals were affixed to a glass capillary with mother liquid and transferred to the goniostat for data collection. Numbers of collected and observed independent [$I > 2\sigma(I)$] reflections are 39 273 and 14 733 ($R_{int} = 0.049$) for **1**, 84 300 and 22 302 ($R_{int} = 0.038$) for **2**, and 10 1732 and 29 142 ($R_{int} = 0.030$) for **3**. The data were integrated using the Siemens SAINT program,[29] with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the

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Table 1. Crystallographic Data for Compounds **1**−**3**

param	**1**·7.5H_2O	**2**·6H_2O	**3**·10H_2O
empirical formula	$C_{84}H_{120}N_6O_{48.5}P_7Mn_{12}$	$C_{114}H_{129}N_6O_{47}P_7Mn_{12}$	$C_{120}H_{143}N_6O_{51}P_7Mn_{12}$
fw	2865.83	3211.34	3361.51
cryst system	monoclinic	monoclinic	monoclinic
space group	Cc	$P2_1/n$	$C2/c$
a (Å)	35.253(17)	16.470(5)	44.499(5)
b (Å)	21.825(11)	48.280(14)	32.321(3)
c (Å)	22.101(11)	20.509(6)	32.849(5)
β (deg)	120.168(11)	105.962(7)	128.703(9)
V (Å^3)	14 701(13)	15 679(8)	36870(9)
Z	2	4	8
D_{cal} (g·cm^3)	1.295	1.360	1.209
μ(Mo Kα) (mm^{-1})	1.139	1.075	0.919
F(000)	5836	6544	13 696
R_1,[a] wR_2[b]	0.0657, 0.1294	0.0585, 0.1324	0.0435, 0.0992
GOF[c]	1.07	1.05	1.08
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$/e·Å^{-3}	0.69, −0.69	1.17, −1.38	0.61, −0.86

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [c] $GOF = [\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obsn} - N_{param})]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound **1**·7.5H_2O

Mn1−O1	1.806(7)	Mn2−O2	1.826(7)	Mn3−O3	1.815(8)
Mn1−O9	1.943(5)	Mn2−O11	2.059(4)	Mn3−O14	2.091(5)
Mn1−O17	2.141(5)	Mn2−O12	1.961(6)	Mn3−O15	1.946(4)
Mn1−O30	2.203(6)	Mn2−O32	2.216(5)	Mn3−O34	2.217(7)
Mn1−N1	2.071(7)	Mn2−N3	2.084(7)	Mn3−N5	2.057(8)
Mn1−N2	2.057(7)	Mn2−N4	2.067(7)	Mn3−N6	2.104(6)
Mn4−O1	2.101(6)	Mn5−O31	1.925(6)	Mn6−O2	2.098(6)
Mn4−O4	1.913(6)	Mn5−O36	2.160(6)	Mn6−O4	1.933(6)
Mn4−O5	1.848(6)	Mn5−O1	1.882(6)	Mn6−O5	2.471(6)
Mn4−O7	2.525(4)	Mn5−O5	1.903(6)	Mn6−O6	1.900(6)
Mn4−O16	1.961(6)	Mn5−O10	2.378(7)	Mn6−O10	1.922(6)
Mn4−O26	1.900(5)	Mn5−O18	1.949(6)	Mn6−O20	1.932(6)
Mn7−O2	1.853(6)	Mn8−O3	2.081(7)	Mn9−O3	1.869(7)
Mn7−O6	1.890(6)	Mn8−O4	1.898(6)	Mn9−O7	1.900(5)
Mn7−O13	2.367(6)	Mn8−O6	2.493(6)	Mn9−O16	2.318(4)
Mn7−O21	1.929(6)	Mn8−O7	1.856(6)	Mn9−O24	1.884(5)
Mn7−O33	1.937(6)	Mn8−O13	1.930(6)	Mn9−O35	1.928(5)
Mn7−O38	2.172(6)	Mn8−O23	1.955(4)	Mn9−O40	2.177(4)
Mn10−O5	1.974(7)	Mn11−O6	1.950(7)	Mn12−O7	1.930(6)
Mn10−O8	1.872(5)	Mn11−O8	1.852(5)	Mn12−O8	1.888(4)
Mn10−O19	2.081(5)	Mn11−O19	2.936(6)	Mn12−O22	2.895(7)
Mn10−O25	2.935(5)	Mn11−O22	2.083(6)	Mn12−O25	2.061(5)
Mn10−O27	1.898(6)	Mn11−O28	1.891(6)	Mn12−O29	1.909(7)
Mn10−O37	1.899(6)	Mn11−O39	1.943(5)	Mn12−O41	1.946(4)
Mn1−O1−Mn5	125.9(3)	Mn8−O4−Mn6	109.4(3)	Mn6−O6−Mn11	119.3(3)
Mn1−O1−Mn4	128.4(3)	Mn4−O4−Mn6	107.6(3)	Mn7−O6−Mn8	95.9(2)
Mn5−O1−Mn4	95.3(2)	Mn4−O5−Mn5	103.5(3)	Mn6−O6−Mn8	89.7(2)
Mn2−O2−Mn7	128.3(3)	Mn4−O5−Mn10	119.0(3)	Mn11−O6−Mn8	117.3(2)
Mn2−O2−Mn6	126.9(3)	Mn5−O5−Mn10	123.6(3)	Mn8−O7−Mn9	103.8(3)
Mn7−O2−Mn6	96.8(2)	Mn4−O5−Mn6	90.7(2)	Mn8−O7−Mn12	121.0(3)
Mn3−O3−Mn9	125.7(3)	Mn5−O5−Mn6	96.1(2)	Mn9−O7−Mn12	123.7(3)
Mn3−O3−Mn8	127.1(3)	Mn10−O5−Mn6	117.2(2)	Mn8−O7−Mn4	89.1(2)
Mn9−O3−Mn8	96.7(3)	Mn7−O6−Mn6	102.7(2)	Mn9−O7−Mn4	94.8(2)
Mn8−O4−Mn4	109.3(2)	Mn7−O6−Mn11	124.6(3)	Mn12−O7−Mn4	116.5(2)
Mn11−O8−Mn10	118.3(3)	Mn11−O8−Mn12	116.9(3)	Mn10−O8−Mn12	117.7(3)
Mn6−O10−Mn5	98.7(2)	Mn8−O13−Mn7	99.0(2)	Mn4−O16−Mn9	99.9(2)

path length through the detector faceplate. Equivalent data were averaged. The structures were solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL.[30] All the non-hydrogen atoms in the three compounds were refined anisotropically. All the hydrogen atoms were placed in calculated positions. Crystallographic and refinement details of compounds **1**−**3** are listed in Table 1, and selected bond lengths and angles of compound **1** are listed in Table 2. Selected bond lengths and angles of complexes **2** and **3** are given in Table S1 and Table S2, respectively.

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Results and Discussion

Syntheses. Through the treatment of $Mn(O_2CMe)_2$·4H_2O with NBu_4MnO_4 in a 4:1 ratio in the presence of acetic acid, Mn^{III} was generated in situ in MeCN:

$$4Mn^{II} + Mn^{VII} \rightarrow 5Mn^{III}$$

This gave a brown solution from which crystals of dodecamanganese cluster $[Mn_{12}O_8(O_2CMe)_6(O_3PC_6H_9)_7(bipy)_3]$·7.5$H_2O$ (**1**·7.5H_2O) were grown on addition of a methanol solution of δ^1-cyclohexenephosphonic acid ($C_6H_9PO_3H_2$) and 2,2′-bipyridine. This one-pot procedure can be readily

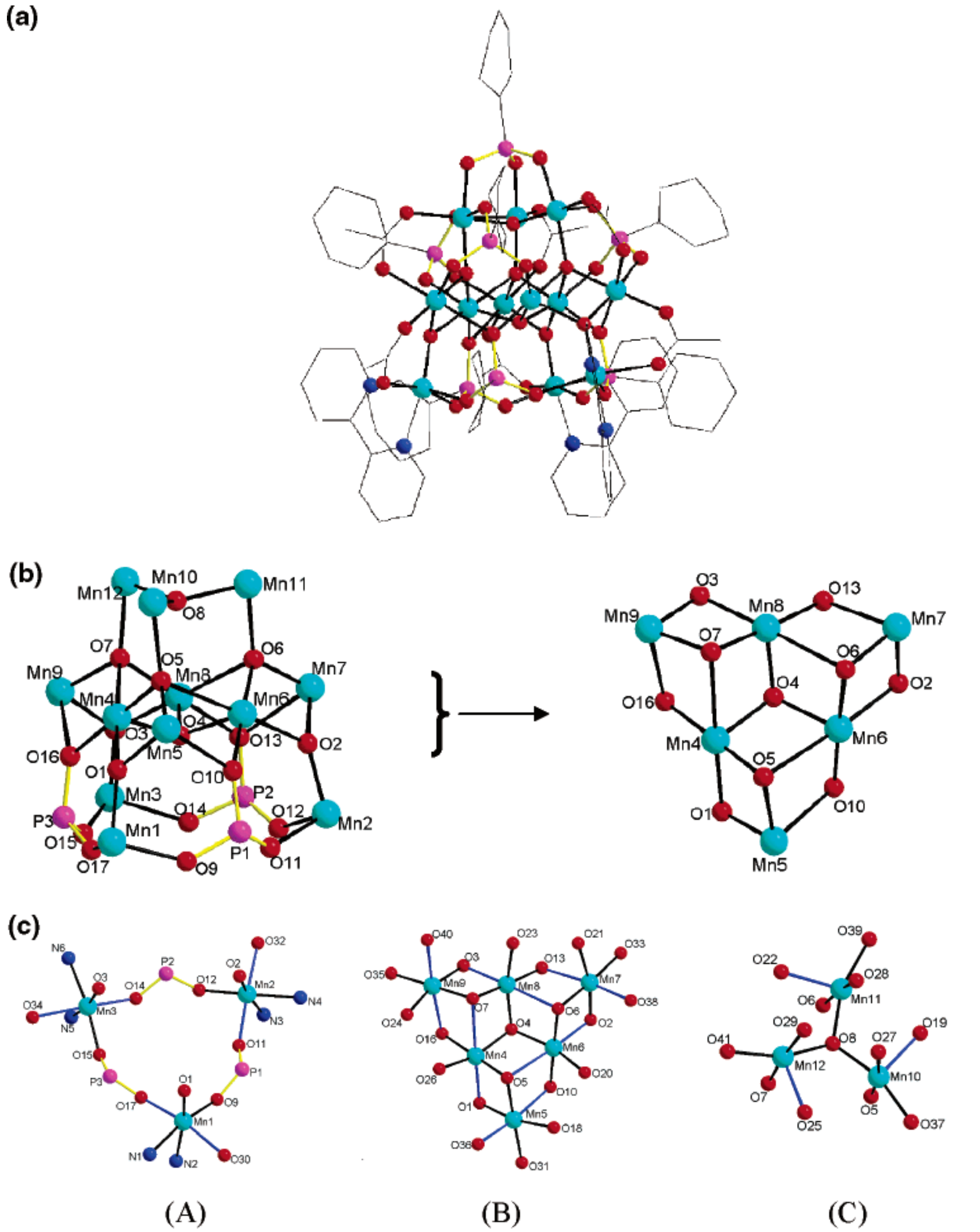


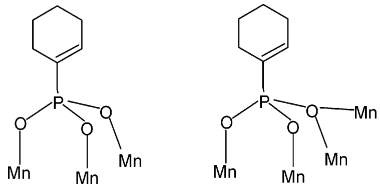
Figure 1. (a) Structure of compound **1**. (b) Mn_{12} core of **1**. (c) Bottom (A), middle (B), and upper (C) layers of the Mn_{12} core of **1**. The Jahn−Teller axes are highlighted with blue color. Color codes: cyan, Mn; purple, P; red, O; blue, N; gray, C.

extended to the preparation of complexes **2** and **3** with formula $[Mn_{12}O_8(O_2CR)_6(O_3PC_6H_9)_7(L)_3]\cdot xH_2O$ (for **2**, R = Ph, L = 2,2-bipy, $x = 5.2$; for **3**, R = Ph, L = 1,10-phen, $x = 10$) by use of $Mn(O_2CPh)_2\cdot 2H_2O$ in place of $Mn(O_2CMe)_2\cdot 4H_2O$ or by use of 1,10-phenanthroline in place of 2,2′-bipyridine. In complexes **1**−**3**, the manganese ions are all in +3 oxidation state. Attempts to further oxidize part of Mn^{III} to Mn^{IV} failed by, for example, changing the ratio of starting material NBu_4MnO_4:$Mn(O_2CMe)_2\cdot 4H_2O$ from 0.25:1 to 0.234:0.5. The XRD pattern of the resulted product is the same as that of compound **1**.

Crystal Structures of 1−3. Figure 1a shows the molecular structure of compound **1** in which all the manganese ions are encased in a lipophilic shell composed of alkyl or phenyl groups protruded from either phosphonate/carboxylate or from 2,2′-bipyridine ligands. The compound contains a $[Mn^{III}_{12}(\mu_4\text{-}O)_3(\mu_3\text{-}O)_5(\mu\text{-}O_3P)_3]$ core (Figure 1b), which may be dissected into three parallel layers of three types (Figure 1c). The bottom layer A consists of three Mn^{III} ions (Mn1, Mn2, Mn3) joining together by three O−P−O bridges, thus forming a 12-member ring. The middle layer B contains six Mn^{III} ions (Mn4, Mn5, Mn6, Mn7, Mn8, Mn9) and can be described as three edge-sharing partial-cubane units. The upper layer C is a Mn^{III}_3 triangular unit (Mn10, Mn11, Mn12) with a $\mu_3\text{-}O^{2-}$ ion (O8) in the center. The A and B layers are connected by three $\mu_3\text{-}O^{2-}$ ions (O1, O2, O3) and three μ_3-O atoms (O10, O13 O16) from three phosphonate ligands. The B and C layers are linked by three $\mu_4\text{-}O^{2-}$ ions (O5, O6, O7).

All the manganese ions in the cluster are in +3 oxidation state, confirmed by the bond valence sum calculation.[31] However, the coordination geometries around the Mn sites

Chart 1



vary. Those in the bottom layer A (Mn1, Mn2, Mn3) have distorted octahedral geometries and O_4N_2 coordination spheres. Octahedral geometries are also found for the Mn^{III} ions in the middle layer B (Mn4, Mn5, Mn6, Mn7, Mn8, Mn9), each of which has six O donors. The Mn sites in the upper layer C (Mn10, Mn11, Mn12) are five-coordinated and have square pyramidal environments. The Jahn−Teller (JT) axially elongated Mn^{III}−O distances are 2.059(4)−2.217(7) Å in layer A, 2.081(7)−2.525(4) Å in layer B, and 2.061(5)−2.083(6) Å in layer C. These are significantly longer than the other Mn^{III}−O distances [1.806(7)−1.974(7) Å]. Unlike the conventional Mn_{12}−O_2CR family, however, there are no parallel anisotropic axes in compound **1**. The JT elongation axes in the upper layer C are all within the plane of the Mn_3 unit, and they are approximately 60° angles to each other. A similar situation is found in the bottom layer A. Although the JT elongation axes in the middle layer B are not within the Mn_6 plane, they have different directions (Figure 1c).

The outer coordination shell of the Mn_{12} core in **1** is occupied by seven $C_6H_5PO_3^{2-}$, six $MeCO_2^-$, and three 2,2′-bipyridine ligands. All carboxylate groups adopt the same η^2-μ-coordination mode. The seven phosphonate groups show two distinct bridging modes: three (in the bottom layer) are each linked to four Mn atoms, while the other four are each connected to three Mn atoms through three phosphonate oxygens (Chart 1). The 2,2′-bipy serves as a terminal ligand and chelates to each of the three Mn atoms in the bottom layer (Mn1, Mn2, Mn3). Figure 2 shows the packing diagram of structure **1** viewed down the *c*-axis. Clearly, the clusters are packed forming a layer in the *bc* plane. The lattice water molecules locate between the layers with extensive hydrogen bond interactions.

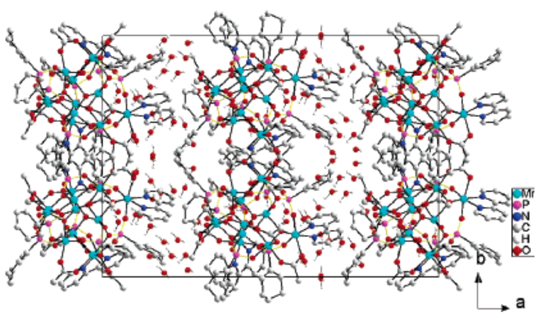
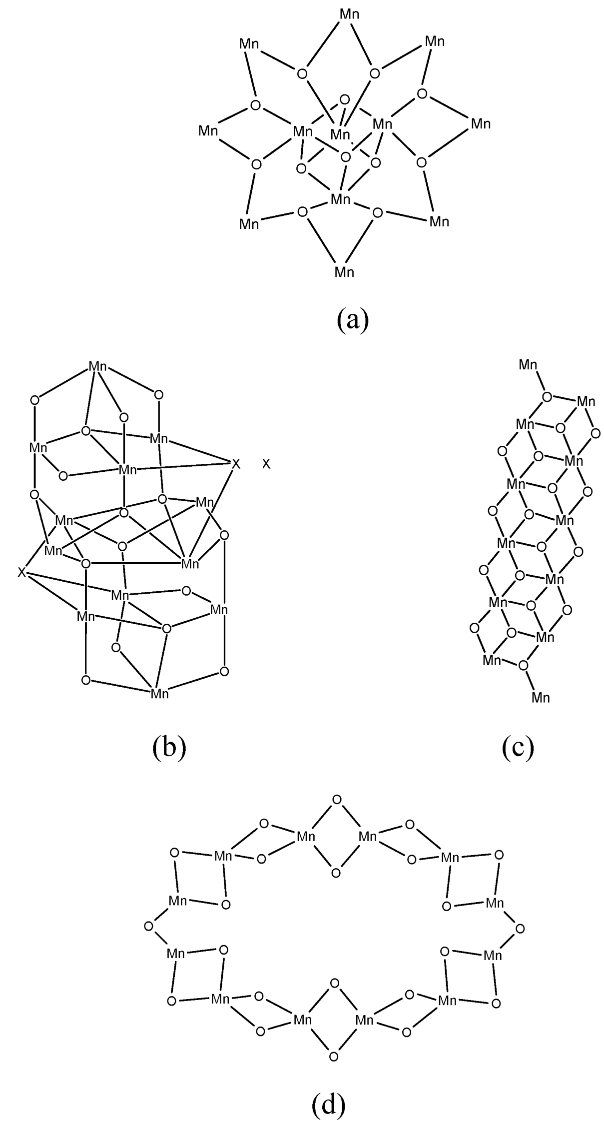


Figure 2. Packing diagram of structure $1 \cdot 7.5H_2O$ viewed down the *c*-axis.

Compounds **2** and **3** have a Mn_{12} core very similar to that of **1**. However, the peripheral ligation for compound **2** consists of seven $C_6H_5PO_3^{2-}$, six $PhCO_2^-$, and three 2,2′-bipyridine ligands. For complex **3**, it is composed of seven $C_6H_5PO_3^{2-}$, six $PhCO_2^-$, and three 1,10-phenanthroline ligands (see Supporting Information).

Chart 2



The Mn_{12} cores in compounds **1**−**3** are significantly different from those in the other dodecamanganese clusters.[3−6] Compounds $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ possess a mixed-valent $[Mn^{III}_8Mn^{IV}_4(\mu_3\text{-}O)_{12}]$ core, with a central $[Mn^{IV}_4O_4]^{8+}$ cubane held within a nonplanar ring of eight Mn^{III} ions by eight μ_3-O^{2-} ions (Chart 2a).[3] Compounds $[Mn_{12}O_8X_4(O_2CPh)_8L_6]$ consist of an $[Mn^{III}_{10}Mn^{II}_2(\mu_4\text{-}O)_4(\mu_3\text{-}O)_4(\mu_2\text{-}O)_8(\mu_3\text{-}X)_2]$ core, comprising three pairs of face-sharing cuboids, i.e., incomplete face-sharing double cubanes (Chart 2b).[4] In $[Mn_{12}O_4(OH)_2(O_2CPh)_{12}(thme)_4(py)_2]$, a mixed-valent $[Mn^{III}_{10}Mn^{II}_2O_4(OH)_2]^{24+}$ ladderlike core is found which can be described as five edge-sharing $[Mn_4O_2]$ butterfly units (Chart 2c).[5] Complexes $[Mn_{12}(O_2CCH_3)_{14}L_4]$ (L = mdea, edea) are also mixed-valent, with six Mn(II) and six Mn(III) ions alternately arranged in a wheel-shaped topology (Chart 2d).[6] Therefore, compounds **1**−**3** with a homovalent $[Mn^{III}_{12}(\mu_4\text{-}O)_3(\mu_3\text{-}O)_5(\mu\text{-}O_3P)_3]$ core provide new examples of dodecamanganese clusters with a new type of topologic structure.

(31) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, *32*, 4102.

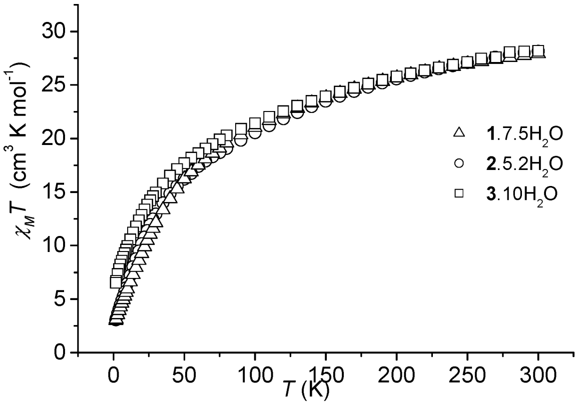


Figure 3. Plots of $\chi_M T$ vs T for complexes **1**·7.5H_2O, **2**·5.2H_2O, and **3**·10H_2O.

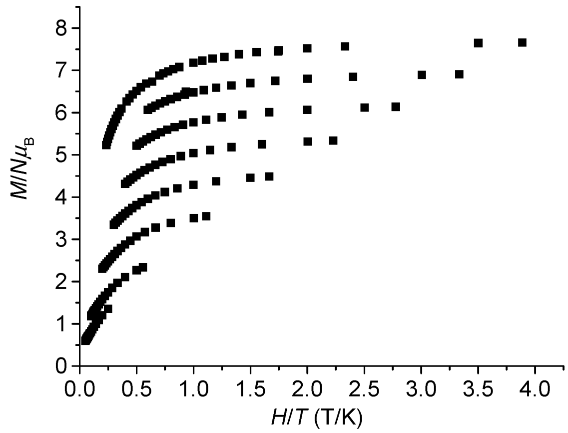


Figure 4. $M/N\mu_B$ versus H/T curve for complex **1**·7.5H_2O.

Magnetic Properties. Temperature-dependent dc magnetic susceptibility measurements were performed on solid samples of complexes **1**−**3** in the temperature range 1.8−300 K in a field of 2 kG. The $\chi_M T$ value of compound **1**·7.5H_2O gradually decreases from 28.14 cm^3 K mol^{-1} at 300 K to 14.83 cm^3 K mol^{-1} at 40 K before falling rapidly to 3.06 cm^3 K mol^{-1} at 1.8 K. For compounds **2**·5.2H_2O and **3**·10H_2O, the $\chi_M T$ values decrease from 28.19 cm^3 K mol^{-1} at 300 K to 6.52 cm^3 K mol^{-1} at 1.8 K for **2**·5.2H_2O, and from 27.94 cm^3 K mol^{-1} at 300 K to 3.01 cm^3 K mol^{-1} at 1.8 K for **3**·10H_2O, respectively (Figure 3). Since the spin-only $\chi_M T$ value for 12 noninteracting Mn^{III} ions is 36 cm^3 K mol^{-1} ($g = 2$), Figure 3 is indicative of an appreciable antiferromagnetic exchange between the Mn^{III} centers in compounds **1**−**3**.

For complexes containing 12 Mn^{III}, the total molecular spin values range from 0 to 24. To determine the spin ground states of complexes **1**−**3**, magnetization data were collected in the temperature range 1.8−7 K and dc magnetic field range 10−70 kG. Figure 4 shows the $M/N\mu_B$ versus H/T curve for complex **1**·7.5H_2O. Suppose that only the ground state is occupied in the measured temperature range; the nonsuperimposable isofields observed in Figure 4 would suggest significant zero-field splitting in the spin-ground state of **1**·7.5H_2O. Unfortunately, it was not possible to obtain a reasonable fit for these data. It seems that low-lying excited states could be populated even at temperatures down to 1.8 K. Low-lying excited states are expected for such a large

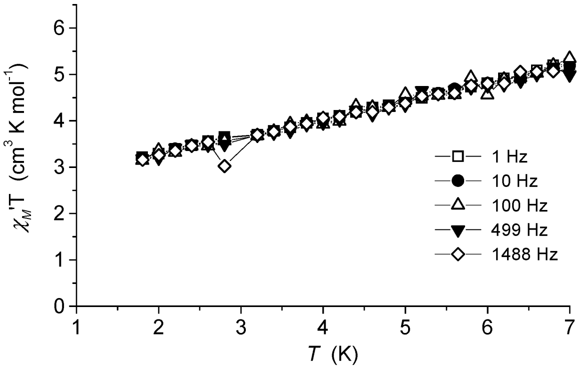


Figure 5. In-phase ($\chi_{M'}T$) ac magnetic susceptibility versus temperature (T) for complex **1**·7.5H_2O.

molecule which usually has a high density of molecular spin states. Besides, the spin frustration effects caused by the extensive presence of Mn_3 triangular units may also lead to small energy differences between the resulting spin states.[32] Similar phenomena had been observed in the other high-nuclearity manganese clusters.[32,33] The ac susceptibility measurements were thus carried out in zero dc field with a 3.0 G ac field oscillating at frequencies 1, 10, 100, 499, and 1488 Hz. Figure 5 shows the in-phase signal $\chi_{M'}T$ versus T curves for complex **1**·7.5H_2O at different frequencies. Indeed, the $\chi_{M'}T$ value decreases with decreasing temperature. Extrapolation of the plot to 0 K gives a $\chi_{M'}T$ value of ca. 2.5 cm^3 K mol^{-1}, suggesting an $S = 2$ ground state with $g = 2.0$. For compounds **2**·5.2H_2O and **3**·10H_2O, the extrapolations give the $\chi_{M'}T$ values of ca. 6.0 and 2.5 cm^3 K mol^{-1}, suggesting the ground states of $S = 3$ and $S = 2$, respectively (Supporting Information).

The out-of-phase signals of complex **1**·7.5H_2O show no peaks down to 1.8 K, and no frequency-dependence of both in-phase and out-of-phase signals were observed. Besides, the ac data are essentially superimposable with the dc data in the temperature range 1.8−7 K. The results indicate that complex **1**·7.5H_2O is not a SMM. Similar magnetic behaviors have been observed for complexes **2**·5.2H_2O and **3**·10H_2O (Supporting Information). The magnetic behaviors of complexes **1**−**3** may be related to their structures. Since the Mn^{III} ions are the main source of the magnetic anisotropy, the orientation of the JT axes of the Mn^{III} ions is crucial to the overall anisotropy of a molecule and thus its magnetic behavior. The JT elongation axes of the Mn^{III} ions in complexes **1**−**3** are not parallel. Instead, they all lie in the layers A, B, or C with different directions (Figure 1c). Therefore, it is not unexpected that complexes **1**−**3** do not show SMM behavior.

It has to be noted that, during the revision of this manuscript, Winpenny et al. reported three new mixed-valent manganese phosphonate compounds with formula $[Et_3NH]_2$-$[Mn^{III}_{18}Mn^{II}_2(\mu_4\text{-}O)_8(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_2(O_3PCH_2Ph)_{12}(O_2CCMe_3)_{10}$-$(py)_2]$, $K_4[Mn^{III}_{16}Mn^{II}_4(\mu_4\text{-}O)_4(\mu_3\text{-}O)_6(O_3PCH_2Ph)_{14}(O_2CPh)_{12}$-$(HO_2CPh)_{0.5}(CH_3CN)_2]$, and $Na_6[Mn^{III}_{14}Mn^{II}_6(\mu_4\text{-}O)_4(\mu_3\text{-}$

(32) King, P.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Inorg. Chem.* **2004**, *43*, 7315.
(33) Chakov, N. E.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Inorg. Chem.* **2004**, *43*, 5919.

$O)_4(OH)_4(O_3PCH_2Ph)_{14}(O_2CPh)_{12}(HO_2CPh)_2(H_2O)_4$-$(CH_3CN)_4$]. All three show unusual SMM behaviors with a high-spin ground state and high coercivity.[34]

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Supporting Information Available: Five tables, eight figures, and X-ray crystallographic files, in CIF format, for the three compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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