

Solvothermal Synthesis and Characterization of Two High-Nuclearity Mixed-Valent Manganese Phosphonate Clusters

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Two novel mixed-valent manganese (Mn^{II}/Mn^{III}) cluster compounds were synthesized in solvothermal reactions and characterized by single-crystal X-ray diffraction, bond valence sum calculations, IR spectra, elemental analysis, and magnetic measurements. Compound **1** is a Mn₁₉ cluster with a cylindrical core structure. Compound **2** possess a Mn₁₆ core where all of the manganese sites have unique ligation environments. The magnetic measurements on both compounds indicate dominant antiferromagnetic interactions between the metal centers.

In the last 10 years, a number of high-nuclearity manganese clusters with interesting properties have been reported in the literature.^{1–6} The possibility of discovering new clusters simply for their structural aesthetics is motivation in itself,

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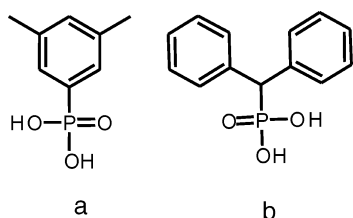
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but the chemistry of high-nuclearity mixed-valent molecular compounds of manganese draws further attention as models for the photosynthetic water oxidation centers⁷ and because of their potential as single-molecule magnets.² Phosphonates (RPO₃²⁻) are versatile ligands that can link metal ions through their three phosphonate oxygen atoms even up to nine metal centers. However, cluster compounds featuring phosphonate ligands are relatively rare. There are a small number of papers previously reported on manganese phosphonate cluster compounds.⁸

Two novel mixed-valent Mn₁₉ and Mn₁₆ clusters, [Mn₁₉(μ₄-O)₆(μ₃-O)₂(O₂CCMe₃)₁₀(OCH₃)₁₆(O₃PPh(Me)₂)₆] (**1**) and [Mn₁₆(Ph₂CHPO₃)₈(μ₄-O)₆(μ₃-O)₂(OMe)₄(HOMe)₂(Me₃CC-O₂)₆(OH₂)(Py)₂] (**2**), were synthesized solvothermally upon reaction of [Mn₃O(Me₃CCO₂)₆(Py)₃]⁹ with 3,5-dimethylphenylphosphonic acid [H₂O₃PPh(Me)₂] and diphenylmethylphosphonic acid [Ph₂CHPO₃H₂], respectively, in methanol at 125 °C for 12 h. The phosphonic acid ligands 3,5-dimethylphenylphosphonic acid and diphenylmethylphosphonic acid (Scheme 1) were synthesized following modified Arbuzov^{10,11} reactions. Syntheses of both of the cluster compounds were first tried in methanol at room temperature.

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Scheme 1



Different organic solvents—acetonitrile, ethanol, and dichloromethane—have also been tried under solvothermal conditions. However, those efforts failed. At room temperature, the yields of the reactions were very low, and because the product compounds were insoluble in most of the common solvents, we were unable to crystallize them. Apparently, high temperature and pressure, as well as the solvent methanol, have a profound role in the synthesis and the ability to crystallize these cluster compounds. That is also revealed by the fact that all of the compounds contain coordinating methanol molecules and bridging methoxides.

Compound **1**^{12a} is a mixed-valent complex, containing 9 Mn^{II} ions and 10 Mn^{III} ions, as determined by bond valence sum (BVS) calculation,¹³ charge considerations, and inspection of the metric parameters. The molecular structure and the core structure of the compound are shown in parts a and b of Figure 1, respectively. The center of the Mn–O core (Figure 2a) consists of a planar isolateral hexagon with six Mn^{III} ions at the corners bonded with a Mn^{II} at the center through six μ_4 -O ions (Figure 2a,b). The lateral distances between manganese ions on the hexagon range from 3.083 to 3.175 Å. The central core is bonded to two pairs of Mn–O triangles stacked one above the another both above and below the Mn7 core (Figure 1b). The oxygen atoms forming the triangles are from phosphonate groups that also connect the triangles to the central core. All of the phosphonate oxygen atoms are involved in this connectivity, and the organic portion of the phosphonic acid groups is outside the cluster. Methoxy groups bridge across manganese atoms on the periphery of the cluster and thus serve an essential role in the formation of the cluster. A total of 12 of the 16 methoxy groups are thereby involved, and the 4 remaining are simply bonded to the manganese atoms at the

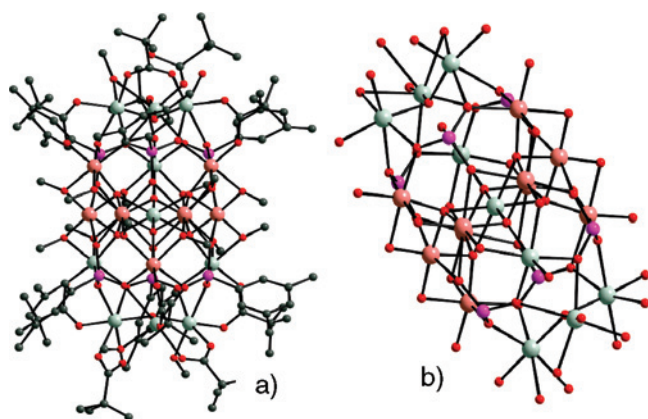


Figure 1. (a) Molecular structure of **1** in the crystal. Color code: pink, Mn^{III}; gray, Mn^{II}; purple, phosphorus; red, oxygen; black, carbon. Hydrogen atoms are omitted for clarity. (b) View of the core structure of **1**. Hydrogen and carbon atoms (in part b) are removed for clarity.

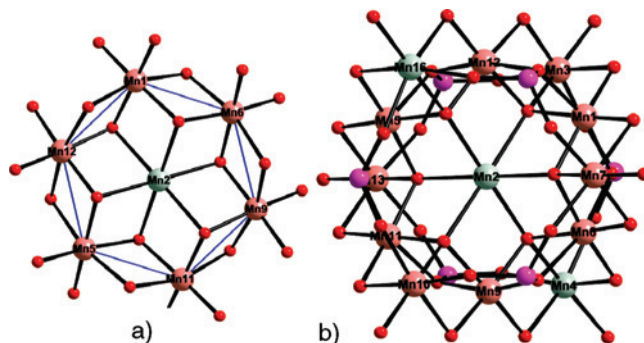


Figure 2. (a) View of the central Mn7 unit in **1**. (b) View of the connectivity of the central manganese in **1** (apex triangles are removed for clarity).

top and bottom of the cluster. The coordination spheres of these manganese atoms are completed by bonding to the trimethylacetate groups. The manganese ions of the central Mn7 unit are held together by 6 μ_4 -O, 12 μ_2 -OCH₃, and 6 μ_3 -O from phosphonates (symmetrically 3 from each side). Interestingly, Mn^{II} at the center is connected with a total of 12 manganese ions (Figure 2b), 6 from the central hexagon and 6 others from the middle triangles on each side through 6 μ_4 -O ions. All of the phosphonates are bonded to a total of six manganese ions, showing a 6.222 topology.¹⁴ The apex triangles are μ_3 -O-centered, and the average distances between manganese atoms are 3.481 and 3.66 Å, which is much less than that of the middle triangles (5.86 and 5.89 Å). The BVS calculations confirm that the manganese atoms in the two apex triangles and one each in the triangles below the outer ones are in the 2+ oxidation state. The central manganese atom is also in the 2+ oxidation state (indicated in gray, Figure 1b). The oxidation state assignments are confirmed by the magnetic susceptibility measurements. The magnetic data of **1** were collected in the temperature range 2–300 K, as shown in the form of a $\chi_M T$ vs temperature (T) plot in Figure 3. The room temperature $\chi_M T$ value for **1** is 60.03 cm³ K mol⁻¹, which is less than the calculated value, 69.37 cm³ K mol⁻¹ ($g = 2$), for 10 Mn^{III} and 9 Mn^{II} noninteracting centers. This behavior is due to the presence of a strong antiferromagnetic interaction, as is expected for this type of large cluster.^{1d} The $\chi_M T$ values decrease smoothly down to 5.85 cm³ K mol⁻¹ upon lowering of the temperature from room temperature to 2 K, as is expected for antiferromagnetic interactions. However, the magnetization experiment for **1** does not show any saturation even at the highest field measured (Figure S1 in the Supporting Information). The possible reason is the presence of low-lying excited

(12) (a) Crystal data for **1**: C₂₂₅H₃₆₀Mn₃₈O₁₂₃P₁₂, $M = 7491.51$, orthorhombic, space group $Pca2_1$, $a = 39.306(5)$ Å, $b = 15.355(2)$ Å, $c = 26.803(4)$ Å, $V = 16177(4)$ Å³, $Z = 4$, $D_c = 1.537$ g cm⁻³, Mo K α radiation, $\lambda = 0.71073$ Å, $T = 110(2)$ K, $2\theta_{max} = 46.7^\circ$, 68 829 reflections collected, 23 251 unique ($R_{int} = 0.0783$). Final GOF = 1.070, $R1 = 0.0620$, $wR2 = 0.1383$, refine_diff_density_max 1.008, refine_diff_density_min -1.063. (b) Crystal data for **2**: C_{297.32}H₃₂₄Mn₃₂N₄O₁₁₇P₁₆, $M = 8075.41$, triclinic, space group $P1$, $a = 18.777(6)$ Å, $b = 20.334(7)$ Å, $c = 25.575(8)$ Å, $\alpha = 79.139(6)^\circ$, $\beta = 75.266(6)^\circ$, $\lambda = 82.242(6)^\circ$, $V = 9236(5)$ Å³, $Z = 2$, $D_c = 1.247$ g cm⁻³, Mo K α radiation, $\gamma = 0.71073$ Å, $T = 110(2)$ K, $2\theta_{max} = 47.1^\circ$, 76 851 reflections collected, 27 241 unique ($R_{int} = 0.0757$). Final GOF = 1.071, $R1 = 0.0821$, $wR2 = 0.2036$, refine_diff_density_max 1.383, refine_diff_density_min -1.220.

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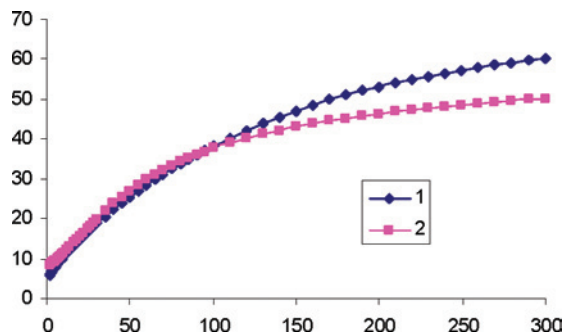


Figure 3. Plot of $\chi_M T$ vs T (2–300 K) plot for **1** and **2**.

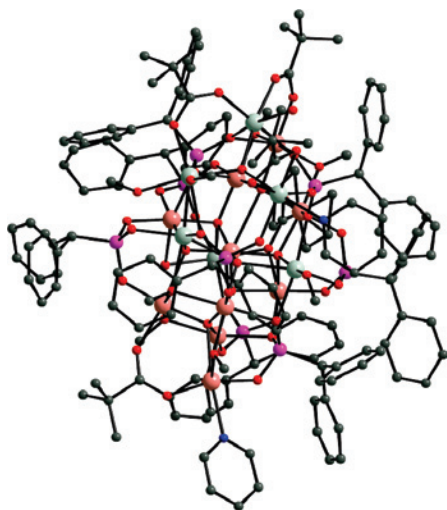


Figure 4. Molecular structure of **2**. Color code: same as that in Figure 1. Hydrogen atoms are removed for clarity.

states, which are populated at higher field or the presence of magnetic spin frustration, because the magnetic structure contains several Mn–O triangles. The dynamic magnetic susceptibility data of **1** were measured by using an alternating current susceptometer. The dynamic susceptibility data (both real and imaginary components; Figures S3 and S4 in the Supporting Information) below 3 K increase upon lowering of the temperature and show frequency dependency. However, the signal is very weak and not well resolved, so no conclusion has been drawn.

Compound **2**^{12b} has 10 Mn^{III} and 6 Mn^{II} centers, as determined from BVS calculations. The X-ray structure analysis of the compound reveals that the Mn–O core has a very irregular shape and is encased in a hydrophobic sheath of alkyl or aryl groups (Figure 4). The Mn–O core can be described as a combination of two subunits, an iso-valent Mn₃–O triangle (Mn13, Mn15, and Mn16 in Figure 5) bonded to a larger Mn₁₃O₇ unit through three phosphonates (in 6.222, 5.221, and 4.211 bridging mode)¹⁴ and one carboxylate group (Figure 5). The Mn₁₃O₇ part can be described based on a central Mn^{II} (Mn2) bonded to five μ_4 -oxides, which are bridged to a total of 10 Mn sites. Mn2 is therefore a vertex of the five O-centered prisms. Two Mn centers, Mn11 and Mn14, are not bridged through any oxo group to the central Mn (Mn2). Mn11 is connected to Mn1 and Mn3 through two OMe and an oxo group, which forms a triangle. Mn14 is bonded to Mn7, Mn10, and Mn14 through one μ_4 -O, two OMe, and a phosphonate group (5.221). The central manganese has a distorted square-

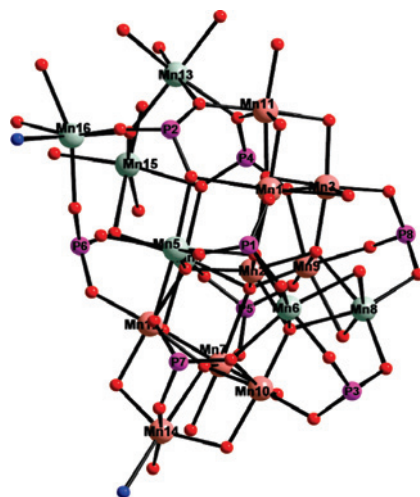


Figure 5. Core structure of **2**. Color code: same as that in Figure 1.

pyramidal geometry, with the longest Mn–O bond [2.138(5) Å] at the apex of the pyramid and all other distances ranging from 1.868(5) to 1.974(5) Å (Table S3 in the Supporting Information). The other 15 manganese atoms are hexacoordinated with distorted octahedral geometry. The hexacoordination of the manganese sites are fulfilled by peripheral ligation of a total of eight OMe groups, eight phosphonate ligands, five carboxylate ligands, and two pyridine molecules. The most interesting feature of the molecule is that all 16 manganese sites are unique based on their ligation.

The susceptibility data for compound **2** were collected in the temperature range 2–300 K, as shown in the form of a $\chi_M T$ vs temperature (T) plot in Figure 3. The room temperature $\chi_M T$ value for **2** is 49.82 cm³ K mol⁻¹, which is much less than the calculated value, 56.25 cm³ K mol⁻¹ (for $g = 2$), for 10 Mn^{III} and 6 Mn^{II} isolated centers. The $\chi_M T$ values decrease smoothly down to 8.316 cm³ K mol⁻¹ upon lowering of the temperature to 2 K, and this indicates the presence of antiferromagnetic interaction between the metal centers. However, like **1**, the magnetization experiment for **2** does not show any saturation even at the highest field measured (Figure S2 in the Supporting Information). The reason for this behavior could also be the same as that discussed for **1**.

In conclusion, we have demonstrated the synthesis and characterization of two large unprecedented mixed-valent manganese cluster compounds. The organic substituent of the phosphonate ligand and the solvent in the reaction have key roles in determining the structural type. This work is currently being extended to other phosphonic acid ligands.

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Supporting Information Available: Syntheses, BVS calculations, selected bond distances, and magnetization curves for **1** and **2**, χ'_M vs T and χ''_M vs T plots for **1**, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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