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Inorganic Chemistry Article

Synthesis of a Mn_6 Cluster and Its Self-Assembly of an Azido-Bridged Polymer[†]

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A rare μ_6-oxo-centered Mn_6 mixed-valent cluster (**1**) is prepared and used as a secondary building unit for the self-assembly of its azido-bridged polymeric analogue (**2**) in a systematic way with the retention of the Mn_6 core of **1**. Both complexes are characterized by X-ray single-crystal structure determination. The complex **1** was crystallized in a monoclinic system, space group $P2_1$, $a = 11.252(5)$ Å, $b = 20.893(9)$ Å, $c = 12.301(6)$ Å, and $\beta = 115.853(7)°$, whereas the polymeric analogue **2** was crystallized in an orthorhombic system, space group $P2_12_12_1$, $a = 13.1941(8)$ Å, $b = 14.9897(9)$ Å, and $c = 27.8746(14)$ Å. Variable-temperature magnetic behavior showed the presence of strong antiferromagnetic interaction in both cases.

Introduction

The research on polynuclear clusters of paramagnetic metal ions has attracted intense study since the discovery of Mn_{12} acetate that showed a slow relaxation of magnetization below a critical temperature.[1a] Moreover, these polymetallic assemblies represent a great synthetic challenge. Two distinct approaches to the synthesis of this kind of complex are designed assembly,[1b−d] in which the use of rigid ligands with a directional bonding approach leads to predesigned structures, and "serendipitous" assembly,[2] in which the ligands are more flexible, and the resulting structures are not predictable. In a majority of the serendipitous assembly syntheses of clusters, carboxylates have been used as the bridging ligands, with a few recent developments where organic di- or trihydroxy bridging ligands along with carboxylate have been used.[2e,2h] The aliphatic hydroxy-based Mn cluster without carboxylate is very rare.[3] The azido anion is also known as a versatile bridging ligand and has been used in the formation of several polymeric networks,[4] where it has been used for the generation of Mn clusters.[5] However, to the best of our knowledge, no example is known where an azido has been used to bridge discrete large clusters in a stepwise manner to form a polymer. Hence, it was of interest to explore the chemistry of a polyhydroxo-based cluster with the incorporation of an azido to link clusters in a controlled way. Herein, we report the synthesis of a rare μ_6-oxo-centered trihydroxy-bridged mixed-valent Mn_6 cluster without a

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[†] This work is dedicated to Profs. George M. Christou and David N. Hendrickson.

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carboxylate coligand (**1**) and its azido-bridged chiral polymeric analogue (**2**) with the retention of the Mn_6 core (Scheme 1)

Scheme 1. Synthesis of Cluster **1** and Its Polymeric Analogue **2**

$$\mathbf{1} \xleftarrow{\text{r.t.}} MnCl_2 + H_3thme + 2NaN_3 \xrightarrow{60\ °C} \mathbf{2}$$

$$\mathbf{1} = Na_2[Mn_6(\mu_6\text{-}O)(thme^{3-})_3(N_3)_5(H_2O)]\cdot 5H_20$$

$$\mathbf{2} = [Na_2\{Mn_6(\mu_6\text{-}O)(thme^{3-})_4(N_3)_4(\mu\text{-}N_3)\}(H_3thme)_2]_n$$

Experimental Section

Materials. 1,1,1-tris(hydroxymethyl)ethane (H_3thme) was purchased from Aldrich and used without further purification. $MnCl_2\cdot 2H_2O$, NaN_3, and solvents were commercially available and used as received.

Physical Measurements. Elemental analyses of C, H, and N were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra taken as KBr pellets were recorded on a Magna 750 FT-IR spectrophotometer. The measurements of variable-temperature magnetic susceptibility and field dependence of magnetization were carried out on a Quantum Design MPMS-XL5 SQUID magnetometer. The experimental susceptibilities were corrected for diamagnetism (Pascal's tables).

Preparation of Complex 1. NaN_3 (2 mmol, 130 mg) was dissolved in 0.5 mL of water and added to the methanolic (10 mL) solution of $MnCl_2\cdot 4H_2O$ (1 mmol, 197.9 mg) and stirred for 10 min to get a small volume of brown-yellow solution to which a methanolic (2 mL) solution of $Me{-}C(CH_2OH)_3$ (1 mmol, 120 mg) was added dropwise, and the clear solution turned into a yellow-brown slurry on the addition of NEt_3 (3 mmol, 0.24 mL) dropwise by a syringe. Then it was stirred for 24 h to get a brown solution with a black-brown precipitate. On evaporation of the brown filtrate, the sample gave very thin and brittle rod-shaped dark-brown-black crystals after 1 week. The crystals became amorphous in a few seconds when removed from the mother liquor. Yield: 35% (based on Mn). Elemental Anal. Calcd for $C_{20}H_{48}N_{15}O_{19}Mn_6Na_2$: C, 21.24; H, 4.25; N, 18.58. Found: C, 21.56; H, 3.89; N, 17.94. IR (KBr): ν (for azide) = 2054 cm^{-1}; ν (for the organic ligand) = 1028, 2929, 2858, 1720, 1249, 823 cm^{-1}.

Preparation of Complex 2. $MnCl_2\cdot 4H_2O$ (4 mmol, 791.6 mg) and NaN_3 (8 mmol, 520 mg) were stirred in Me−OH (10 mL) at 60 °C for 1 h in the presence of open air to obtain a brown slurry to which a methanolic (5 mL) solution of $Me{-}C(CH_2OH)_3$ (4 mmol, 480 mg) was added dropwise over a period of 5 min. Then the mixture was stirred for 30 min followed by dilution to 30 mL and stirred for 3 h to get a dark-brown solution. The dark-brown filtrate was dried in reduced pressure, and the brown mass was extracted with THF (THF = tetrahydrofuran). Brown single crystals were obtained by the diffusion of ether into the THF solution. Yield: 26%. Elemental Anal. Calcd for $C_{30}H_{60}Mn_6N_{15}Na_2O_{19}$: C, 27.48; H, 4.58; N, 16.03. Found: C, 27.80; H, 4.86; N, 16.33. IR (KBr): ν (for azide) = 2064 cm^{-1}; ν (for the organic ligand) = 3431, 1022, 2929, 2862, 1629, 1119, 609 cm^{-1}.

Crystal Structure Determinations. The crystal data for **1** were collected using a Bruker SMART APEX CCD diffractometer, equipped with a fine-focus sealed-tube Mo Kα X-ray source. The *SMART* program was used for data acquisition, and the *SAINT* program was used for data extraction. For **2,** data collection was performed using a Mo Kα radiation using the Oxford Diffraction X-Calibur CCD system. The crystals were positioned 50 mm from the CCD. Frames numbering 321 were measured with a counting time of 10 s. Data analysis was carried out with the *Crysalis*[8] program. The structures were solved using direct methods with the *SHELX-97* program.[6] The non-hydrogen atoms were refined with anisotropic thermal parameters. The disordered atoms were refined with constrained dimensions. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. An absorption correction was carried out using the *ABSPACK*[9] program. One terminal azide of **2** was disordered over two sites with occupancies 0.54(1), 0.46(1). Also present in the asymmetric unit were three methanol and two water molecules all refined with 25% occupancy. The structures were refined on F^2 using *SHELX-97*.

Table 1. Crystal Data and Structure Refinement Parameters for **1** and **2**

	compound	
	1	**2**
empirical formula	$C_{21}H_{52}Mn_6$-$N_{15}Na_2O_{21}$	$C_{30.75}H_{57.75}Mn_6$-$N_{15}Na_2O_{20.25}$
fw	1226.40	1337.29
T/K	150(2)	150(2)
space group	$P2_1$	$P2_12_12_1$
a/Å	11.252(5)	13.194(8)
b/Å	20.893(9)	14.989(9)
c/Å	12.301(6)	27.874(14)
α/deg	90.00	90.00
β/deg	115.853(7)	90.00
γ/deg	90.00	90.00
V/Å^3	2602.0(2)	5512.9 (5)
Z	2	4
μ(Mo−Kα)/mm^{-1}	0.857	0.704
λ/Å	0.71073	0.71073
R^a	0.1060	0.0597
$R_w{}^b$	0.2728	0.1155
D/Mg m^{-3}	1.17	1.16

$^a\ R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b\ R_w = [\Sigma\{w(F_o{}^2 - F_c{}^2)^2\}/\Sigma\{w(F_o{}^2)^2\}]^{1/2}$.

Results and Discussion

Synthesis. The reaction between $MnCl_2$ and H_3thme in the presence of NaN_3 gives $Na_2[Mn_6(\mu_6\text{-}O)(thme)_3(N_3)_5(H_2O)]$ (**1**) in 35% isolated yield. This complex was crystallographically identified as **1**$\cdot 5H_2O$. Given that the starting manganese source contains only Mn^{II} ion, it is clear that the Mn^{III} ions are formed by aerial oxidation upon stirring for long time, as observed by the slow color change from light yellow to dark brown. The paramagnetic complex part of **1** is anionic, and the charge of this complex part is neutralized by two Na^+ counterions. The oxidation of Mn^{II} is mediated by air. A similar reaction was repeated without the presence of oxygen, but this yielded only a white slurry (indicative of the presence of only Mn^{II} ions), which could not be characterized. Our primary attempt was to remove the coordinated labile water, followed by the linking of the sixth Mn of this cluster, by one of the pendant azides from the neighboring cluster to obtain a polymer of **1** in a controlled way. Interestingly, when the same reaction was performed under reflux, the coordinated water molecule was

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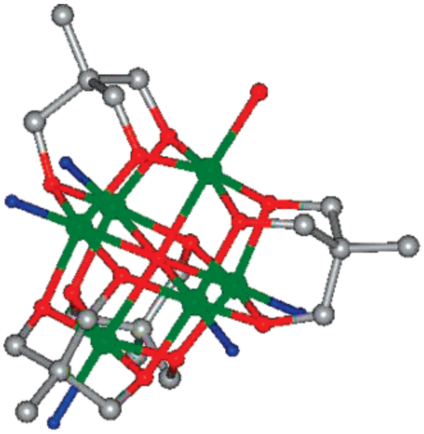

Figure 1. Molecular structure of complex **1** (green = Mn; gray = C; red = O; blue = N).

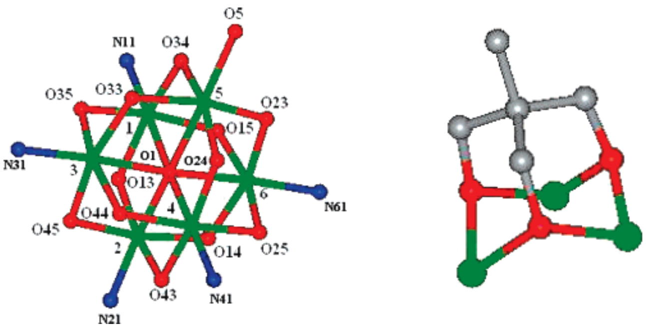

Figure 2. View of the Mn_6O_{13} core of **1** with atom numbering (left); blue atoms represent the coordinated nitrogen atoms of azides, and O5 is the oxygen of coordinated water. Bridging mode of the $thme^{3-}$ anion (right).

removed and the expected azido-linking polymeric analogue of **1** was isolated in 26% yield (complex **2**). We believe that the use of NaN_3 is also very important for the formation of complexes **1** and **2**, and it may have a role in the deprotonation of the H_3thme ligand as well in balancing the charge of the anionic complex ion. The proposed overall reactions for the formation of **1** and **2** are summarized in eqs 1 and 2, respectively.

$$12MnCl_2 + 8H_3thme + 10NaN_3 + {}^5/_2O_2 + 18Et_3N + 3H_2O \rightarrow 2[Na_2Mn_6(O)(thme)_4(N_3)_5(H_2O)_6] + 6NaCl + 18Et_3N{\cdot}HCl \quad (1)$$

$$12MnCl_2 + 12H_3thme + 10NaN_3 + {}^5/_2O_2 \rightarrow 2[Na_2Mn_6(O)(thme)_4(H_3thme)_2(N_3)_5(H_2O)_3] + 6NaCl + 18HCl \quad (2)$$

Crystal Structure of 1. Complex **1** is a μ_6-oxo-centered Mn_6 cluster with one pendant azide on each of the five Mn ions and a water molecule on the axial position of the sixth Mn. The compound **1** was obtained as deep-brown crystals by the diffusion of ether into a brown methanolic solution. The crystals are soluble in THF and CH_2Cl_2 and lose crystalline nature in a few seconds if taken out of the mother liquor. X-ray single-crystal structure analysis clearly demonstrated that the cluster contains four bridging $thme^{3-}$ anions and six manganese atoms with a central μ_6-O^{2-} coordinated to six manganese ions in an octahedral geometry. A view of the octahedral core is shown in Figure 1.

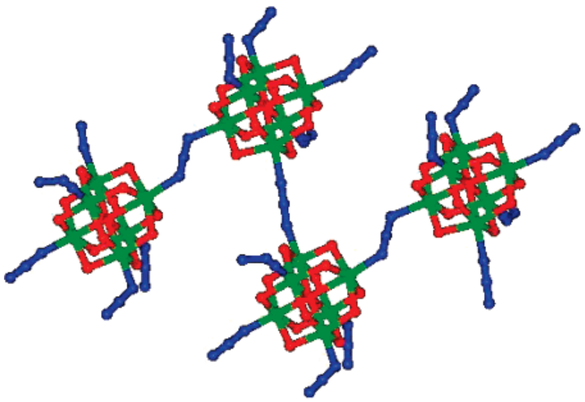

Figure 3. View of the azido-bridged 1D chain unit in complex **2**.

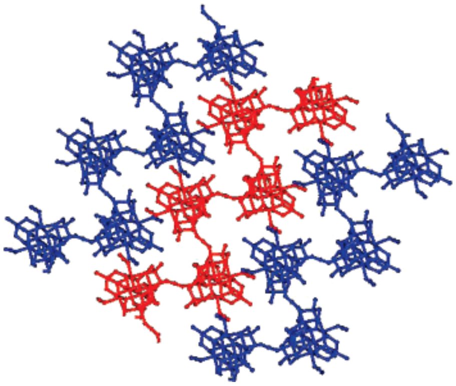

Figure 4. Packing view of neighboring chains in complex **2**.

The Mn_6 core can be described as an octahedron with a μ_6-O^{2-}atom at the center of the octahedron (Figure 2). The alternative triangular faces of this octahedron are occupied by bridging $thme^{3-}$ ligands as if forming a Mn_3-based adamantanoid-type unit. The six Mn ions in the cluster are all six-coordinate with near-octahedral geometry. Each of the five Mn atoms is coordinated to a pendant azide anion whereas the other manganese (Mn(5)) is coordinated to a water. Two Na^+ counterions and five water molecules were found in the crystal lattice. The coordination environments around the sodium ions were satisfied by the waters of crystallization and weak interaction from the alkoxo oxygen of the $thme^{3-}$.

Crystal Structure of 2. The single-crystal structure analysis of **2** revealed an one-dimensional (1D) zigzag chain formed by linking the Mn_6 cores through an end-to-end azide. The repeating secondary building unit in this complex is a Mn_6O_{13} core similar to the octahedron core of complex **1**. One end nitrogen (N(13)) of the pendant azido on Mn(1) was linked to the newly created empty axial position on the Mn(5) atom of the neighboring cluster. A view of the zigzag chain unit in **2** is shown in Figure 3.

This complex was crystallized with two more molecules of the free H_3thme ligand and two Na^+ counterions. Finally, Na^+ and H_3thme as well as other pendant azide ligands extended the neighboring 1D zigzag chains in **2** to a three-dimensional (3D) assembly (see the Supporting Information and Figure 4). A view of the packing of 1D chains in the solid state is shown in Figure 4. H-bonding among the chains through H_3thme stabilized the final polymeric structure. The

Table 2. Bond-Valence Calculations for Complex **2**[a]

A_i	B_j	bond (r_{ij}) length (Å)	S_{ij}	ΣS_{ij}	conclusion
Mn(1)	O(1)	2.289	0.198	2.371	Mn^{II}
Mn(1)	O(13)	2.121	0.408		
Mn(1)	O(15)	2.079	0.458		
Mn(1)	O(34)	2.123	0.406		
Mn(1)	O(35)	2.115	0.415		
Mn(1)	N(11)	2.123	0.486		
Mn(2)	O(1)	2.301	0.231	3.131	Mn^{III}
Mn(2)	O(13)	1.934	0.624		
Mn(2)	O(14)	1.928	0.635		
Mn(2)	O(43)	1.956	0.588		
Mn(2)	O(45)	1.942	0.611		
Mn(2)	N(21)	2.134	0.442		
Mn(3)	O(1)	2.281	0.244	2.984	Mn^{III}
Mn(3)	O(33)	2.074	0.427		
Mn(3)	O(35)	1.924	0.641		
Mn(3)	O(44)	1.920	0.648		
Mn(3)	O(45)	2.015	0.415		
Mn(3)	N(31)	2.215	0.609		
Mn(4)	O(1)	1.962	0.579	3.064	Mn^{III}
Mn(4)	O(24)	2.101	0.398		
Mn(4)	O(25)	2.006	0.514		
Mn(4)	O(43)	2.163	0.440		
Mn(4)	O(44)	2.001	0.431		
Mn(4)	N(41)	1.947	0.732		
Mn(5)	O(1)	2.259	0.259	3.158	Mn^{III}
Mn(5)	O(23)	1.916	0.655		
Mn(5)	O(24)	1.931	0.629		
Mn(5)	O(33)	1.935	0.623		
Mn(5)	O (34)	1.929	0.633		
Mn(5)	N(13)	2.211	0.359		
Mn(6)	O(1)	2.242	0.272	2.961	Mn^{III}
Mn(6)	O(14)	2.057	0.413		
Mn(6)	O(15)	1.912	0.663		
Mn(6)	O(23)	2.006	0.392		
Mn(6)	O(25)	1.951	0.597		
Mn(6)	N(61)	2.116	0.624		

[a] Where $S = \exp[(r_o - r_{ij})/B]$; $B = 0.37$; r_o = empirically determined parameters.

3D packing view showed the formation of nanochannels in the structure.

With the consideration of the total charge balance as well as the bond-valence calculations, these complexes are assumed to be Mn^{II}Mn$^{III}{}_5$ mixed-valent systems. The bond-valence calculations of complex **2** and selected bond parameters of both the complexes are assembled in Tables 2 and 3, respectively. As expected, the Mn^{III} ions showed Jahn–Teller elongations in both complexes. For example, Mn(1) in complex **2** was assumed to be Mn^{II} due to it having no distinct Jahn–Teller elongation, while the other Mn ions showed axial elongations (Table 2). Similarly, Mn(6) in complex **1** is assumed to be Mn^{II} (Table 3).

Magnetic Properties. The variable-temperature solid-state direct current magnetic susceptibility data for both complexes were collected in the temperature range of 2–300 K in an applied field of 1 kG. In both cases, antiferromagnetic interaction was noticed. Plots of $\chi_M T$ versus T data for **1** and **2** per Mn$_6$ unit are presented in Figure 5.

The $\chi_M T$ values for **1** and **2** at room temperature are 13.8 and 14.9 cm^3 mol^{-1} K, respectively. These values are less than the expected average value for five uncoupled high-spin Mn^{III} ($S = 2$) and a high-spin Mn^{II} ($S = {}^5/_2$). The $\chi_M T$ values for **1** gradually fall from 13.8 cm^3 mol^{-1} K at 300 K to 2.9 cm^3 mol^{-1} K at 2 K, the rate of decrease increasing below 100 K. Similarly, for **2** also the $\chi_M T$ values gradually fall from 14.9 cm^3 mol^{-1} K at 300 K to 3.2 cm^3 mol^{-1} K at 2 K. The $\chi_M T$ values, as well as the nature of curves, are characteristic of a strong antiferromagnetically coupled system. The $\chi_M{}^{-1}$ versus T data plot showed the deviation from linearity below 70 K. The $\chi_M{}^{-1}$ versus T data for both complexes were fitted well with the Curie–Weiss equation down to 70 K, and below this temperature the experimental curves deviated from linearity. The calculated C and θ values are 18.52 cm^3 mol^{-1} K and -102 K for **1** and 20.53 cm^3 mol^{-1} K and -86 K for **2**, respectively. The high negative θ values in both cases confirmed the existence of strong antiferromagnetic interactions. The slight difference in the absolute values of $\chi_M T$ of these two complexes is presumably due to their difference in molecular composition as well as interchain interaction in **2** through the Na$^+$ counterions, since no such intermolecular interaction was found in **1**. The field-dependent magnetization data for both complexes are shown in Figure 6, and no saturation in magnetization values was observed. The ground spin state of **1** was calculated to be $S = 2$. The electron paramagnetic resonance (EPR) spectrum of **1** showed no signal at room temperature. However, at low temperature (<25 K) this complex showed EPR activity. The doubled derivative of absorbance (a) vs applied magnetic field (H) plot showed two sets of peaks. The expanded form of the peak at 3353 G showed the presence of six closely

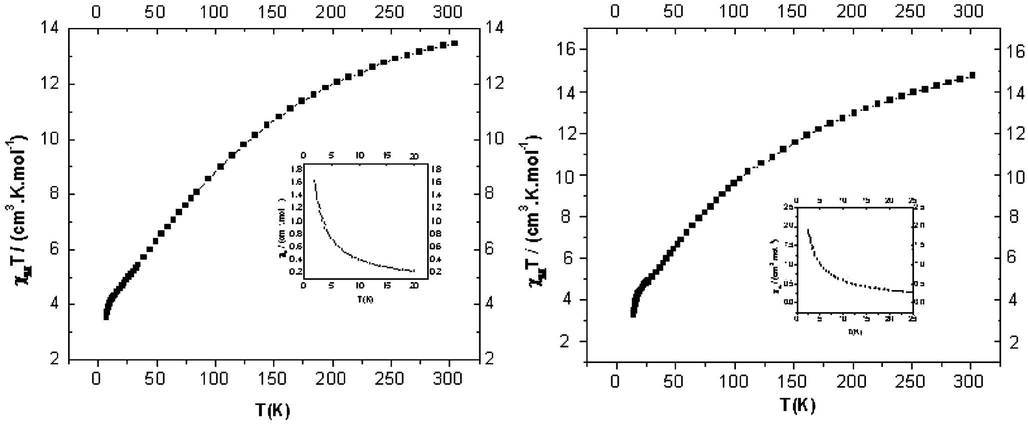

Figure 5. $\chi_M T$ versus T plots for **1** (left) and **2** (right). Plots of χ_M versus T at the low-temperature region are shown in insets.

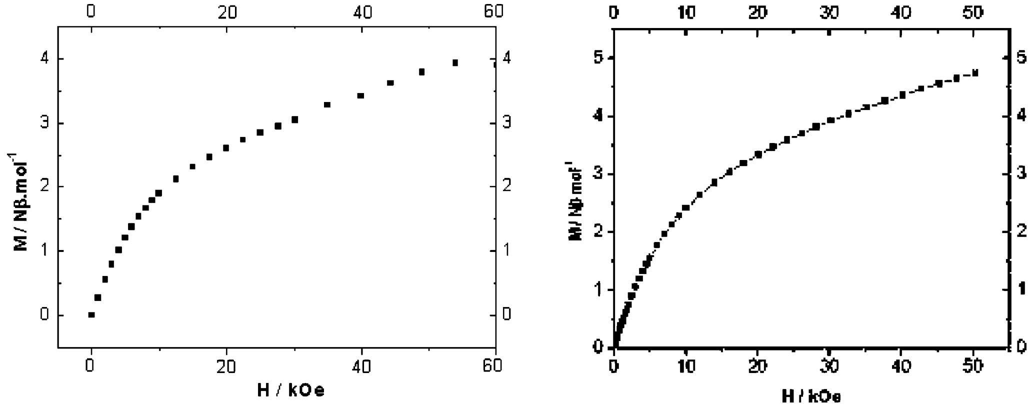

Figure 6. *M* versus *H* plot at 2 K for **1** (left) and **2** (right).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**

		1			
Mn(1)−O(1)	2.129(17)	Mn(1)−O(13)	2.267(14)	Mn(1)−O(15)	1.998(11)
Mn(1)−O(34)	2.952(12)	Mn(1)−O(35)	2.002(12)	Mn(1)−N(11)	2.030(18)
Mn(2)−O(1)	2.189(11)	Mn(2)−O(13)	1.990(14)	Mn(2)−O(14)	1.942(12)
Mn(2)−O(43)	1.963(10)	Mn(2)−O(45)	1.992(12)	Mn(2)−N(23)	2.112(16)
Mn(3)−O(1)	2.287(14)	Mn(3)−O(33)	2.055(13)	Mn(3)−O(35)	2.022(13)
Mn(3)−O(44)	2.048(12)	Mn(3)−O(45)	2.042(13)	Mn(3)−N(31)	2.174(18)
Mn(4)−O(1)	2.129(17)	Mn(4)−O(24)	2.015(12)	Mn(4)−O(25)	1.998(13)
Mn(4)−O(43)	2.055(13)	Mn(4)−O(44)	2.002(12)	Mn(4)−N(41)	2.172(16)
Mn(5)−O(1)	2.373(11)	Mn(5)−O(23)	1.920(13)	Mn(5)−O(24)	1.955(11)
Mn(5)−O(33)	1.946(12)	Mn(5)−O(34)	1.955(13)	Mn(5)−O(5)	2.303(16)
Mn(6)−O(1)	2.196(14)	Mn(6)−O(14)	2.062(14)	Mn(6)−O(15)	1.991(12)
Mn(6)−O(23)	2.063(12)	Mn(6)−O(25)	2.038(13)	Mn(6)−N(61)	2.018(16)
N(13)−N(12)−N(11)	174.4(3)	Mn(2)−O(1)−Mn(1)	92.3(5)		
Mn(1)−O(1)−Mn(4)	176.3(6)	Mn(2)−O(3)−Mn(1)	102.4(5)		
Mn(1)−O(15)−Mn(6)	103.5(5)	Mn(2)−O(14)−Mn(6)	104.3(5)		
Mn(4)−O(25)−Mn(6)	102.6(5)	Mn(2)−O(3)−Mn(1)	102.4(5)		
Mn(5)−O(24)−Mn(4)	107.3(5)	Mn(5)−O(23)−Mn(6)	106.9(5)		
Mn(1)−O(35)−Mn(3)	104.0(6)	Mn(5)−O(34)−Mn(1)	106.0(5)		
		2			
N(13)−N(12)−N(11)	179.0(6)	Mn(2)−O(1)−Mn(1)	86.8(13)		
Mn(1)−O(1)−Mn(4)	179.6(4)	Mn(2)−O(13)−Mn(1)	102.4(5)		
Mn(1)−O(1)−Mn(2)	86.8(13)	Mn(5)−O(24)−Mn(4)	99.8(16)		
Mn(6)−O(25)−Mn(4)	101.1(2)	Mn(5)−O(33)−Mn(3)	106.05(18)		
Mn(3)−O(35)−Mn(1)	105.56(18)	Mn(2)−O(14)−Mn(6)	105.11(18)		
Mn(1)−O(15)−Mn(1)	105.66(17)	Mn(5)−O(23)−Mn(6)	105.42(16)		

spaced lines due to Mn^{II}. The calculated *g* value is 1.99, and the *A* values are 84.273, 89.755, 89.792, 91.54, and 92.090 G.

In summary, the combination of azide and trihydroxy alcohol in a manganese cluster has yielded a rare μ_6-oxo-centered Mn_6 octahedron without a carboxylate coligand. A similar reaction at a relatively higher temperature yielded an azido-linking poly cluster with the retention of the Mn_6 core. Winpenny and co-workers recently introduced phosphonates as couplers to grow carboxylate-based Fe_3 triangles to larger discrete clusters.[7] Moreover, Brechin et al. have also shown that Mn_3 triangles can be assembled to larger arrays using polyhydroxy ligands.[2h−j] Our present results suggest that an azido could be used to link cages into polymeric arrays by displacement reaction with the retention of the primary core. The use of azido groups or other pseudohalide linkers in conjunction with a high-spin ground state cluster and the formation of a poly cluster have the potential to considerably expand this field by making possible the observation of the change in properties of the parent cluster upon the formation of the polymer.

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Supporting Information Available: X-ray crystallographic files (CIFs) for both complexes and packing diagram of complex **2** and the EPR spectra of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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